10/508792
DT12 Rec'd PCT/PTO 21 SEP 2004

SPECIFICATION

INK SET FOR INKJET RECORDING AND INKJET RECORDING METHOD

TECHNICAL FIELD

The present invention relates to an inkjet recording ink and a recording method using the ink, more specifically, the present invention relates to an ink set for inkjet recording and an inkjet recording method, which can ensure high pictorial quality of recording image and excellent preservability of the image obtained.

BACKGROUND ART

Accompanying recent popularization of computers, an inkjet printer is widely used for printing letters or drawing an image on paper, film, cloth or the like not only at offices but also at homes.

The inkjet recording method includes a system of jetting out a liquid droplet by applying a pressure from a piezoelectric element, a system of jetting out a liquid droplet by generating a bubble in the ink under heat, a system of using an ultrasonic wave, and a system of jetting out a liquid droplet by suction using an electrostatic force. The inkjet recording ink used therefor includes an aqueous ink, an oily ink and a solid (fusion-type) ink.

Among these inks, an aqueous ink is relatively superior to oily ink or solid (fusion-type) ink in view of possibility of satisfying all of production, handleability, odor, safety and the like and therefore, is predominating as the inkjet recording ink at present.

The colorant used in such an inkjet recording ink is required to have high solubility in a solvent (ink medium), enable high-density recording, provide good color hue, exhibit excellent fastness to light, heat, air, water and chemicals, ensure good fixing to an image-receiving material and less bleeding, give an ink having excellent storability, have high purity and no toxicity, and be available at a low cost. Various dyes and pigments for use in inkjet recording have been already proposed and are actually used, but a colorant satisfying all of the requirements described above is not yet found out at present.

Conventionally well-known dyes and pigments such as colorant having a color index (C.I.) number can hardly satisfy all of those various properties required of the inkjet recording ink.

As for the dye capable of improving the fastness, azo dyes derived from an aromatic amine and a 5-membered heterocyclic amine have been proposed in Patent Document 1. However, these dyes have a problem of bad color

reproducibility due to undesirable color hue present in the yellow and cyan regions. Patent Documents 2 and 3 are disclosing an inkjet recording ink with an attempt to enhance the light fastness. However, in use as a water-soluble ink, the colorants used in these patent publications are insufficient in the solubility in water, as a result, satisfactory pictorial quality and gradation cannot be obtained. Also, if the water solubility is high, there arises a problem in the fastness of ink to humidity and heat.

In order to solve these problems, compounds and ink compositions described in Patent Document 4 have been proposed. Furthermore, an inkjet recording ink using a pyrazolylaniline azo dye for improving the color hue and light fastness is described in Patent Document 5. However, these inkjet recording inks are still insufficient to satisfy both the pictorial quality and the fastness of the image output.

With recent spreading of inkjet print, it is strongly demanded to satisfy both the highly refined inkjet image and the image preservability. More specifically, the former requires to enhance particularly the pictorial quality and the latter requires to improve particularly the resistance against heat, light and oxidative atmosphere.

For enhancing the pictorial quality, an inkjet

recording method of performing recording by using dark and pale two inks differing in the drawing density has been proposed and is actually used. When multiple inks differing in the kind of dye or in the concentration are used, rich gradation is attained for the halftone of image drawn and the gradation region is also enlarged, as a result, the pictorial quality is enhanced in this point, but in the high density region and the low density region, that is, the shadow part and the highlight part, in many cases, gradation is not reproduced and also change in the color hue is liable to occur, as a result, the pictorial quality is rather deteriorated in this point. It is found that this deterioration of pictorial quality is in a level incapable of correcting by a software for image adjustment of an inkjet printer and must be solved by the ink design.

Out of those various properties required of the inkjet recording ink, it is not yet sufficiently attained to satisfy both excellent image preservability against light, heat and high humidity and excellent pictorial quality of the image drawn, and realization thereof is demanded on the market.

[List of Patent Documents as Background Art]

The above-described technical documents as the background art are as follows.

[Patent Document 1]

JP-A-55-161856 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")

[Patent Document 2] JP-A-61-36362

[Patent Document 3] JP-A-2-212566

[Patent Document 4]

JP-T-11-504958 (the term "JP-T" as used herein means a "published Japanese translation of a PCT patent application")

[Patent Document 5]

Japanese Patent Application No. 2000-80733

An object of the present invention is to solve the problems of inkjet recording ink described above in the item of Background Art, more specifically, to provide an ink set for inkjet recording and an inkjet recording method, which can ensure high pictorial quality of recording image and also excellent preservability of the image obtained.

DISCLOSURE OF THE INVENTION

The object of the present invention can be attained by the ink set for inkjet recording described in the following (1) to (9). This ink set for inkjet recording is used for performing inkjet recording by the method described in (10) to (14) below. In particular, the effect

of the present invention is remarkably brought out when the image recording is performed on the image-receiving layer of the image recording material described in (13) or (14).

(1). An ink set comprising plural inks for inkjet, each one of the plural inks having a maximum absorption wavelength of one of from 500 to 580 nm and from 580 to 680 nm in an aqueous medium and a different absorbance,

wherein based on an absorbance of a dye (or a combination of dyes) in an ink, which has a maximum dye concentration out of the plural inks, an absorbance of a dye (or a combination of dyes)in all another ink excepting the ink having a maximum dye concentration is from 1/20 to 1/2.

(2). The ink set for inkjet recording as described in (1), wherein each one of the plural inks has a maximum absorption wavelength of from 500 to 580 nm in an aqueous medium.

(3). The ink set for inkjet recording as described in (2), wherein out of dyes contained in an ink having a maximum dye concentration in the plural inks constituting the ink set, a dye having a maximum absorbance is an azo dye having a chromophore represented by the following formula:

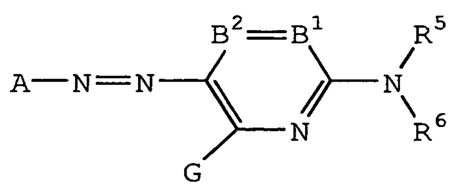
[(heterocyclic ring A)-N=N-(heterocyclic ring B)]

wherein the heterocyclic ring A and the heterocyclic B may have the same structure.

(4). The ink set for inkjet recording as described in (3), wherein the azo dye having a chromophore represented by the formula [(heterocyclic ring A)-N=N-(heterocyclic ring B)] is a colorant having an oxidation potential of more positive than 0.7 V (vs SCE).

(5). The ink set for inkjet recording as described in any one of (2) to (4), wherein the azo dye is a dye represented by the following formula (1):

Formula (1):



wherein A represents a 5-membered heterocyclic group;

B^1 and B^2 each represents $=CR^1-$ or $-CR^2=$ or either one of B^1 and B^2 represents a nitrogen atom and other represents $=CR^1-$ or $-CR^2=$;

R^5 and R^6 each independently represents a hydrogen atom or a substituent, the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a

carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and the hydrogen atom of each substituent may be substituted;

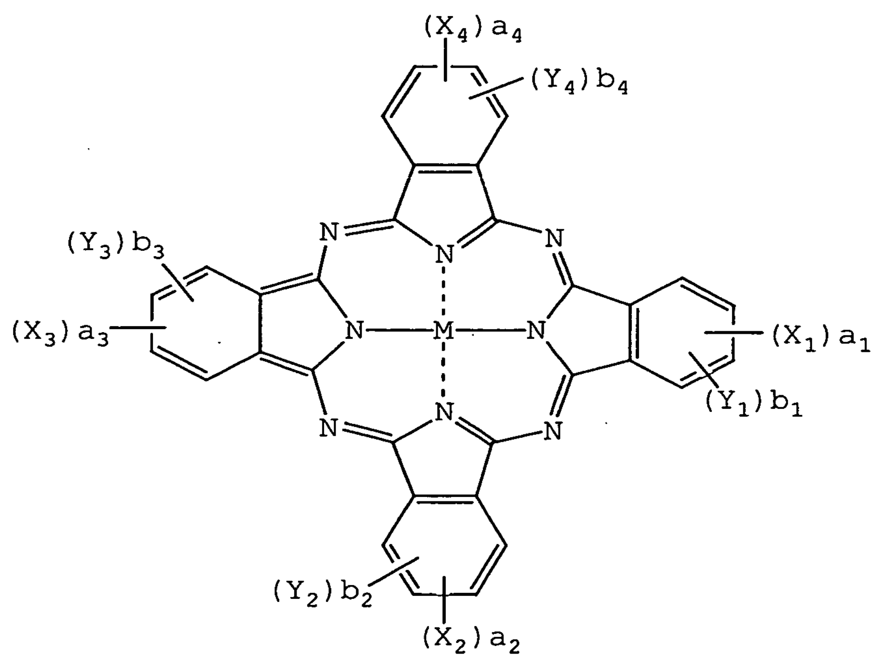
G, R^1 and R^2 each independently represents a hydrogen atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and the hydrogen atom of each substituent may be substituted; and

R^1 and R^5, or R^5 and R^6 may combine to form a 5- or 6-membered ring.

(6). The ink set for inkjet recording as described in (1), wherein each one of the plural inks has a maximum absorption wavelength of from 580 to 680 nm in the aqueous medium.

(7). The ink set for inkjet recording as described in (6), wherein out of dyes contained in an ink having a maximum dye concentration in the plural inks constituting the ink set, a dye having a maximum absorbance is a dye represented by the following formula (I):

Formula (I):



wherein X_1, X_2, X_3 and X_4 each independently represents -SO-Z, $-SO_2-Z$, $-SO_2NR_1R_2$, a sulfo group, $-CONR_1R_2$ or $-CO_2R_1$,

(wherein Z represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a

substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, and R_1 and R_2 each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, provided that when multiple Zs are present, these may be the same or different),

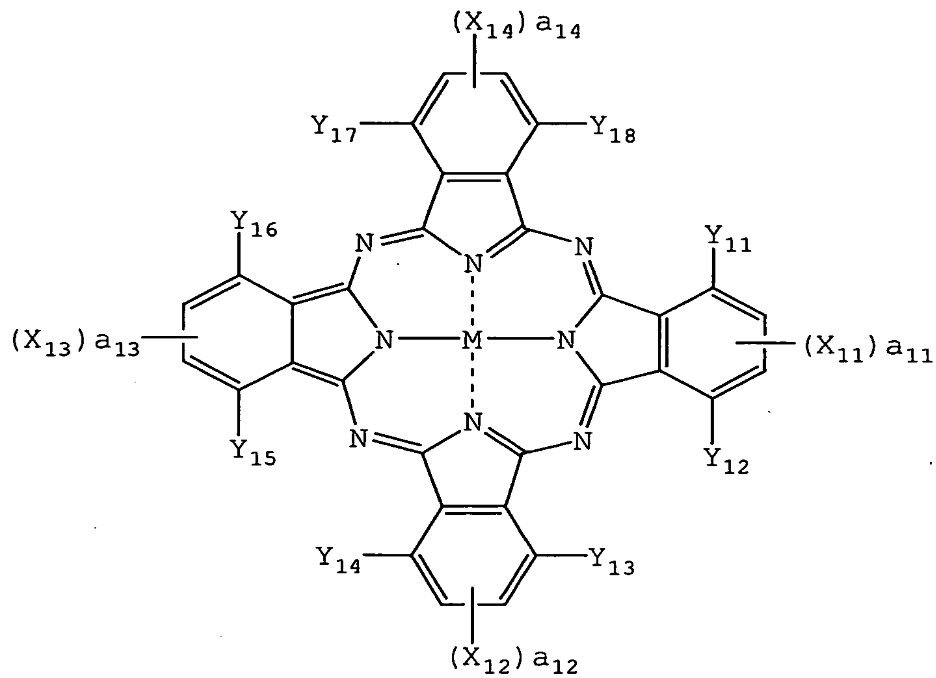
Y_1, Y_2, Y_3 and Y_4 each independently represents a monovalent substituent,provided that when multiple X_1s, X_2s, X_3s, X_4s, Y_1s, Y_2s, Y_3s or Y_4s are present, these may be the same or different,

a_1 to a_4 and b_1 to b_4 represent the number of substituents of X_1 to X_4 and Y_1 to Y_4, respectively, a_1 to a_4 each independently represents 0 or an integer of 1 to 4 but all are not 0 at the same time, b_1 to b_4 each independently represents 0 or an integer of 1 to 4, and

M represents a hydrogen atom, a metal atom or an oxide, hydroxide or halide thereof.

(8). The ink set for inkjet recording as described in (7), wherein the dye represented by formula (I) is a dye represented by the following formula (II):

Formula (II):



wherein X_{11} to X_{14}, Y_{11} to Y_{18} and M have the same meanings as X_1 to X_4, Y_1 to Y_4 and M in formula (I), respectively, and

a_{11} to a_{14} each independently represents an integer of 1 or 2.

(9). The ink set for inkjet recording as described in (7) or (8), wherein the dye represented by formula (I) is a colorant having an oxidation potential of more positive than 0.7 V (vs SCE).

(10). An inkjet recording method, which uses the ink set as described in any one of (1) to (9).

(11). The inkjet recording method as described in 10, which uses the ink set described in any one of (2) to (5).

(12). The inkjet recording method as described in (10), which uses the ink set described in any one of (6) to (9).

(13). The inkjet recording method as described in (10) to (12), wherein an image is recorded by ejecting ink droplets according to recording signals on an image-receiving material, which comprises a support and an image-receiving layer containing an inorganic white pigment particle on the support.

(14). The inkjet recording method as described in (13), wherein the image-receiving layer comprises the inorganic white pigment particle and at least one aqueous binder selected from polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, gelatin, carboxyalkyl cellulose, casein and polyvinylpyrrolidone.

That is, the present invention is an ink set comprising inks including an aqueous medium, which is an ink set comprising an ink having a main absorption region of 500 to 580 nm, that is, a magenta ink, or an ink set comprising an ink having a main absorption region of 580 to 680 nm, that is, a cyan ink, wherein in either case, based on the absorbance of a dye (or a combination of dyes) in an ink having a maximum dye concentration out of multiple inkjet inks constituting the ink set, the absorbance of a dye (or a combination of dyes) in other constituent inks is

adjusted to from 1/20 to 1/2. By virtue of such a design for the ink set, the disturbance in gradation of high density part (shadow part) and low density part (highlight part) and the change in color hue can be prevented from occurring, the pictorial quality of recording image can be kept high, and the obtained image can have excellent preservability, whereby the object of the present invention can be attained. The absorbance as used herein is an absorbance measured for light through a Status A green or blue filter combined with a C standard light source having approximation to average daylight.

For successfully bringing out the effect of the present invention, it is effective to use, regarding the dye for a magenta ink set, the azo dye represented by formula (1) as the main dye for an ink in the high density side and, regarding the dye for a cyan ink set, use the phthalocyanine dye represented by formula (I), particularly formula (II), as the main dye for an ink in the high density side.

Also, in order to bring out excellent image preservability, the azo dye represented by the formula [(heterocyclic ring A)-N=N-(heterocyclic ring B)] and the cyan dye represented by formula (I) each preferably has an oxidation potential of more positive than 0.7 V (vs SCE). When a main dye having such a high oxidation potential is

present, the image obtained by combining it with another colorant having the same main absorption region can have fastness and the image preservability is enhanced.

One or more of two colorants used in combination may be a pigment or sparingly soluble dye which is insoluble in an aqueous ink medium and added to the composition by emulsion-dispersion.

BEST MODE FOR CARRYING OUT THE INVENTION

Specific embodiments of the present invention are described in detail below.

In the present invention, the term "colorant" is used when collectively indicating a dye and a pigment.

<Colorants Sharing Main Absorption Region of 500 to 580 nm>

In order to satisfy the objective properties of the present invention for the inkjet recording ink, that is, excellent weather resistance, ensured color hue and superior pictorial quality, as for the magenta ink, an ink having characteristic features specified in (1) to (6) above is used for image recording. Accordingly, the properties of the magenta dye contained in the ink are described below.

Fundamentally, the magenta ink used for the inkjet recording ink of the present invention is preferably an ink containing a colorant having an absorption maximum in the

spectral region of 500 to 580 nm in an aqueous medium, particularly, an ink comprising an aqueous medium having dissolved or dispersed therein a magenta dye selected from azo dyes, and the azo dye is preferably a dye having an oxidation potential of more positive than 0.7 V (vs SCE).

The first preferred structural feature of this azo dye is that the dye has a chromophore represented by the formula: (heterocyclic ring A)-N=N-(heterocyclic ring B). In this case, the heterocyclic rings A and B may have the same structure. Specifically, the heterocyclic rings A and B each is a 5- or 6-membered heterocyclic ring selected from pyrazole, imidazole, triazole, oxazole, thiazole, selenazole, pyridone, pyrazine, pyrimidine and pyridine. These are specifically described, for example, in Japanese Patent Application Nos. 2000-15853 and 2001-15614, JP-A-2002-309116 and Japanese Patent Application No. 2001-195014.

The second preferred structural feature of the azo dye is that an aromatic nitrogen-containing 6-membered heterocyclic ring is bonded as a coupling component directly to at least one side of the azo group. Specific examples thereof are described in Japanese Patent Application No. 2001-110457.

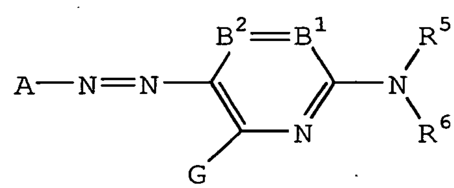
The third preferred structural feature is that the auxochrome has an aromatic ring amino group or heterocyclic amino group structure, specifically, an anilino group or a

heterylamino group.

The fourth preferred structural feature is that the dye has a steric structure. This is specifically described in Japanese Patent Application No. 2002-12015.

Among these preferred structural features of the azo dye, the dye most preferred for achieving the object of the present invention is a dye represented by the following formula (1).

Formula (1):



wherein A represents a 5-membered heterocyclic group;

B^1 and B^2 each represents $=CR^1-$ or $-CR^2=$ or either one of B^1 and B^2 represents a nitrogen atom and the other represents $=CR^1-$ or $-CR^2=$;

R^5 and R^6 each independently represents a hydrogen atom or a substituent, the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and the hydrogen atom of each substituent may be substituted;

G, R^1 and R^2 each independently represents a hydrogen

atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and the hydrogen atom of each substituent may be substituted; and

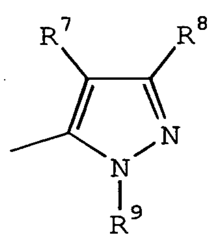
R^1 and R^5, or R^5 and R^6 may combine to form a 5- or 6-membered ring.

The dye of formula (1) is described in more detail.

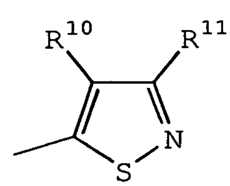
In formula (1), A represents a 5-membered heterocyclic group. Examples of the heteroatom of the heterocyclic ring include N, O and S. A is preferably a

nitrogen-containing 5-membered heterocyclic ring and the heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or another heterocyclic ring. Preferred examples of the heterocyclic ring represented by A include a pyrazole ring, an imidazole ring, a thiazole ring, an isothiazole ring, a thiadiazole ring, a benzothiazole ring, a benzoxazole ring and a benzisothiazole ring. Each heterocyclic group may further have a substituent. Among these rings, more preferred are a pyrazole ring, an imidazole ring, an isothiazole ring, a thiadiazole ring and a benzothiazole ring represented by the following formulae (a) to (f):

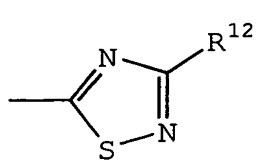
Formula (a)



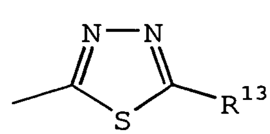
(b)



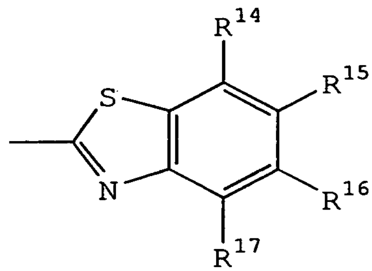
(c)



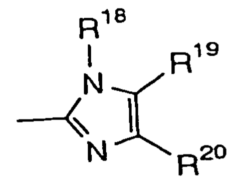
(d)



(e)



(f)



wherein R^7 to R^{20} each represents the same substituent as G, R^1 and R^2 in formula (1).

Among formulae (a) to (f), preferred are a pyrazole ring and an isothiazole ring represented by formulae (a) and (b), and most preferred is a pyrazole ring represented by formula (a).

In formula (1), B^1 and B^2 each represents $=CR^1-$ or $-CR^2=$ or either one of B^1 and B^2 represents a nitrogen atom and the other represents $=CR^1-$ or $-CR^2=$. B^1 and B^2 each preferably represents $=CR^1-$ or $-CR^2=$.

R^5 and R^6 each independently represents a hydrogen atom or a substituent, the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and the hydrogen atom of each substituent may be substituted.

R^5 and R^6 each is preferably a hydrogen atom, an

aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group, and the hydrogen atom of each substituent may be substituted, but R^5 and R^6 are not a hydrogen atom at the same time.

G, R^1 and R^2 each independently represents a hydrogen atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an

arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and the hydrogen atom of each substituent may be substituted.

G is preferably a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy group, a heterocyclic oxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxy-carbonylamino group, an aryloxycarbonylamino group, an alkylthio group, an arylthio group or a heterocyclic thio group, more preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy group, an amino group or an acylamino group, and most preferably a hydrogen atom, an amino group (preferably an anilino group) or an acylamino group, and the hydrogen atom of each substituent may be substituted.

R^1 and R^2 each is preferably a hydrogen atom, an alkyl group, a halogen atom, an alkoxycarbonyl group, a carboxyl group, a carbamoyl group, a hydroxy group, an alkoxy group or a cyano group, and the hydrogen atom of each substituent may be substituted.

R^1 and R^5, or R^5 and R^6 may combine to form a 5- or 6-membered ring.

When A has a substituent or when the substituent R^1, R^2, R^5, R^6 or G further has a substituent, examples of the

substituent include the substituents described above for G, R^1 and R^2.

In the case where the dye of the present invention is a water-soluble dye, the dye preferably further has an ionic hydrophilic group as a substituent at any position on A, R^1, R^2, R^5, R^6 and G. Examples of the ionic hydrophilic group as a substituent include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium).

The terms (substituents) used in the present invention are described below. These terms each is common among different symbols in formula (1) and also in formula (1a) shown later.

The halogen atom includes a fluorine atom, a chlorine atom and a bromine atom.

The aliphatic group means an alkyl group, a substituted alkyl group, an alkenyl group, a substituted

alkenyl group, an alkynyl group, a substituted alkynyl group, an aralkyl group and a substituted aralkyl group. The "substituted" used for a "substituted alkyl group" and the like in the present invention means that the hydrogen atom present in an "alkyl group" or the like is substituted, for example, by a substituent described above for G, R^1 and R^2.

The aliphatic group may be branched or may form a ring. The number of carbon atoms in the aliphatic group is preferably from 1 to 20, more preferably from 1 to 16. The aryl moiety in the aralkyl group and in the substituted aralkyl group is preferably a phenyl group or a naphthyl group, more preferably a phenyl group. Examples of the aliphatic group include a methyl group, an ethyl group, a butyl group, an isopropyl group, a tert-butyl group, a hydroxyethyl group, a methoxyethyl group, a cyanoethyl group, a trifluoromethyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a cyclohexyl group, a benzyl group, a 2-phenethyl group, a vinyl group and an allyl group.

The aromatic group means an aryl group and a substituted aryl group. The aryl group is preferably a phenyl group or a naphthyl group, more preferably a phenyl group. The number of carbon atoms in the aromatic group is preferably from 6 to 20, more preferably from 6 to 16.

Examples of the aromatic group include a phenyl group,

a p-tolyl group, a p-methoxyphenyl group, an o-chlorophenyl group and an m-(3-sulfopropylamino)phenyl group.

The heterocyclic group includes a substituted heterocyclic group. In the heterocyclic group, the heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or another heterocyclic ring. The heterocyclic group is preferably a 5- or 6-membered heterocyclic group. Examples of the substituent of the substituted heterocyclic group include an aliphatic group, a halogen atom, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfamoyl group, a carbamoyl group and an ionic hydrophilic group. Examples of the heterocyclic group include a 2-pyridyl group, a 2-thienyl group, a 2-thiazolyl group, a 2-benzothiazolyl group, a 2-benzoxazolyl group and a 2-furyl group.

The carbamoyl group includes a substituted carbamoyl group. Examples of the substituent therefor include an alkyl group. Examples of the carbamoyl group include a methylcarbamoyl group and a dimethylcarbamoyl group.

The alkoxycarbonyl group includes a substituted alkoxycarbonyl group. The alkoxycarbonyl group is preferably an alkoxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted alkoxycarbonyl group include an ionic hydrophilic group. Examples of the alkoxycarbonyl group

include a methoxycarbonyl group and an ethoxycarbonyl group.

The aryloxycarbonyl group includes a substituted aryloxycarbonyl group. The aryloxycarbonyl group is preferably an aryloxycarbonyl group having from 7 to 20 carbon atoms. Examples of the substituent of the substituted aryloxycarbonyl group include an ionic hydrophilic group. Examples of the aryloxycarbonyl group include a phenoxycarbonyl group.

The heterocyclic oxycarbonyl group includes a substituted heterocyclic oxycarbonyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic oxycarbonyl group is preferably a heterocyclic oxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic oxycarbonyl group include an ionic hydrophilic group. Examples of the heterocyclic oxycarbonyl group include a 2-pyridyloxycarbonyl group.

The acyl group includes a substituted acyl group. The acyl group is preferably an acyl group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted acyl group include an ionic hydrophilic group. Examples of the acyl group include an acetyl group and a benzoyl group.

The alkoxy group includes a substituted alkoxy group.

The alkoxy group is preferably an alkoxy group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted alkoxy group include an alkoxy group, a hydroxyl group and an ionic hydrophilic group. Examples of the alkoxy group include a methoxy group, an ethoxy group, an isopropoxy group, a methoxyethoxy group, a hydroxyethoxy group and a 3-carboxypropoxy group.

The aryloxy group includes a substituted aryloxy group. The aryloxy group is preferably an aryloxy group having from 6 to 20 carbon atoms. Examples of the substituent of the substituted aryloxy group include an alkoxy group and an ionic hydrophilic group. Examples of the aryloxy group include a phenoxy group, a p-methoxyphenoxy group and an o-methoxyphenoxy group.

The heterocyclic oxy group includes a substituted heterocyclic oxy group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic oxy group is preferably a heterocyclic oxy group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic oxy group include an alkyl group, an alkoxy group and an ionic hydrophilic group. Examples of the heterocyclic oxy group include a 3-pyridyloxy group and a 3-thienyloxy group.

The silyloxy group is preferably a silyloxy group

substituted by an aliphatic or aromatic group having from 1 to 20 carbon atoms. Examples of the silyloxy group include a trimethylsilyloxy group and a diphenylmethylsilyloxy group.

The acyloxy group includes a substituted acyloxy group. The acyloxy group is preferably an acyloxy group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted acyloxy group include an ionic hydrophilic group. Examples of the acyloxy group include an acetoxy group and a benzoyloxy group.

The carbamoyloxy group includes a substituted carbamoyloxy group. Examples of the substituent therefor include an alkyl group. Examples of the carbamoyloxy group include an N-methylcarbamoyloxy group.

The alkoxycarbonyloxy group includes a substituted alkoxycarbonyloxy group. The alkoxycarbonyloxy group is preferably an alkoxycarbonyloxy group having from 2 to 20 carbon atoms. Examples of the alkoxycarbonyloxy group include a methoxycarbonyloxy group and an isopropoxy-carbonyloxy group.

The aryloxycarbonyloxy group includes a substituted aryloxycarbonyloxy group. The aryloxycarbonyloxy group is preferably an aryloxycarbonyloxy group having from 7 to 20 carbon atoms. Examples of the aryloxycarbonyloxy group include a phenoxycarbonyloxy group.

The amino group includes a substituted amino group. Examples of the substituent therefor include an alkyl group, an aryl group and a heterocyclic group, and the alkyl group, the aryl group and the heterocyclic group each may further have a substituent. The alkylamino group includes a substituted alkylamino group. The alkylamino group is preferably an alkylamino group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted alkylamino group include an ionic hydrophilic group. Examples of the alkylamino group include a methylamino group and a diethylamino group.

The arylamino group includes a substituted arylamino group. The arylamino group is preferably an arylamino group having from 6 to 20 carbon atoms. Examples of the substituent of the substituted arylamino group include a halogen atom and an ionic hydrophilic group. Examples of the arylamino group include a phenylamino group and a 2-chlorophenylamino group.

The heterocyclic amino group includes a substituted heterocyclic amino group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic amino group is preferably a heterocyclic amino group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic amino group include an alkyl group,

a halogen atom and an ionic hydrophilic group.

The acylamino group includes a substituted acylamino group. The acylamino group is preferably an acylamino group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted acylamino group include an ionic hydrophilic group. Examples of the acylamino group include an acetylamino group, a propionylamino group, a benzoylamino group, an N-phenylacetylamino group and a 3,5-disulfobenzoylamino group.

The ureido group includes a substituted ureido group. The ureido group is preferably a ureido group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted ureido group include an alkyl group and an aryl group. Examples of the ureido group include a 3-methylureido group, a 3,3-dimethylureido group and a 3-phenylureido group.

The sulfamoylamino group includes a substituted sulfamoylamino group. Examples of the substituent therefor include an alkyl group. Examples of the sulfamoylamino group include an N,N-dipropylsulfamoylamino group.

The alkoxycarbonylamino group includes a substituted alkoxycarbonylamino group. The alkoxycarbonylamino group is preferably an alkoxycarbonylamino group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted alkoxycarbonylamino group include an ionic

hydrophilic group. Examples of the alkoxycarbonylamino group include an ethoxycarbonylamino group.

The aryloxycarbonylamino group includes a substituted aryloxycarbonylamino group. The aryloxycarbonylamino group is preferably an aryloxycarbonylamino group having from 7 to 20 carbon atoms. Examples of the substituent of the substituted aryloxycarbonylamino group include an ionic hydrophilic group. Examples of the aryloxycarbonylamino group include a phenoxycarbonylamino group.

The alkylsulfonylamino group and the arylsulfonylamino group include a substituted alkylsulfonylamino group and a substituted arylsulfonylamino group, respectively. The alkylsulfonylamino group and the arylsulfonylamino group are preferably an alkylsulfonylamino group having from 1 to 20 carbon atoms and an arylsulfonylamino group having from 1 to 20 carbon atoms, respectively. Examples of the substituent of the substituted alkylsulfonylamino group and substituted arylsulfonylamino group include an ionic hydrophilic group. Examples of the alkylsulfonylamino group and arylsulfonylamino group include a methylsufonylamino group, an N-phenyl-methylsulfonylamino group, a phenylsulfonylamino group and a 3-carboxyphenylsulfonylamino group.

The heterocyclic sulfonylamino group includes a substituted heterocyclic sulfonylamino group. Examples of

the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic sulfonylamino group is preferably a heterocyclic sulfonylamino group having from 1 to 12 carbon atoms. Examples of the substituent of the substituted heterocyclic sulfonylamino group include an ionic hydrophilic group. Examples of the heterocyclic sulfonyl-amino group include a 2-thienylsulfonylamino group and a 3-pyridylsulfonylamino group.

The alkylthio group, the arylthio group and the heterocyclic thio group include a substituted alkylthio group, a substituted arylthio group and a substituted heterocyclic thio group, respectively. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The alkylthio group, the arylthio group and the heterocyclic thio group are preferably an alkylthio group having from 1 to 20 carbon atoms, an arylthio group having from 1 to 20 carbon atoms and a heterocyclic thio group having from 1 to 20 carbon atoms, respectively. Examples of the substituent of the substituted alkylthio group, substituted arylthio group and substituted heterocyclic thio group include an ionic hydrophilic group. Examples of the alkylthio group, arylthio group and heterocyclic thio group include a methylthio group, a phenylthio group and a 2-pyridylthio

group.

The alkylsulfonyl group and the arylsulfonyl group include a substituted alkylsulfonyl group and a substituted arylsulfonyl group, respectively. Examples of the alkylsulfonyl group and arylsulfonyl group include a methylsulfonyl group and a phenylsulfonyl group.

The heterocyclic sulfonyl group includes a substituted heterocyclic sulfonyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic sulfonyl group is preferably a heterocyclic sulfonyl group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic sulfonyl group include an ionic hydrophilic group. Examples of the heterocyclic sulfonyl group include a 2-thienylsulfonyl group and a 3-pyridylsulfonyl group.

The alkylsulfinyl group and the arylsulfinyl group include a substituted alkylsulfinyl group and a substituted arylsulfinyl group, respectively. Examples of the alkylsulfinyl group and arylsulfinyl group include a methylsulfinyl group and a phenylsulfinyl group.

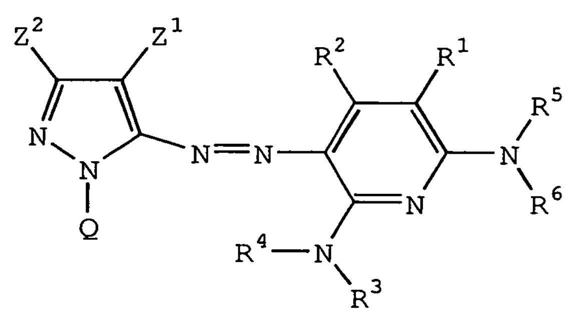
The heterocyclic sulfinyl group includes a substituted heterocyclic sulfinyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic

sulfinyl group is preferably a heterocyclic sulfinyl group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic sulfinyl group include an ionic hydrophilic group. Examples of the heterocyclic sulfinyl group include a 4-pyridylsulfinyl group.

The sulfamoyl group includes a substituted sulfamoyl group. Examples of the substituent therefor include an alkyl group. Examples of the sulfamoyl group include a dimethylsulfamoyl group and a di-(2-hydroxyethyl)sulfamoyl group.

Among those represented by formula (1), particularly preferred is a structure represented by the following formula (1a):

Formula (1a):



In formula (1a), R^1, R^2, R^5 and R^6 have the same meanings as in formula (1).

R^5 and R^4 each independently represents a hydrogen atom or a substituent and the substituent is an aliphatic

group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group or a heterocyclic group.

Z^1 represents an electron-withdrawing group having a Hammett's substituent constant σp value of 0.20 or more. Z^1 is preferably an electron-withdrawing group having a σp value of 0.30 or more, more preferably 0.45 or more, still more preferably 0.60 to more, but the σp value preferably does not exceed 1.0. Specific preferred examples of this substituent include electron-withdrawing substituents described later. Among those, preferred are an acyl group having from 2 to 20 carbon atoms, an alkyloxycarbonyl group having from 2 to 20 carbon atoms, a nitro group, a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms, an arylsulfonyl group having from 6 to 20 carbon atoms, a carbamoyl group having from 1 to 20 carbon atoms and a halogenated alkyl group having from 1 to 20 carbon atoms, more preferred are a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms and an arylsulfonyl group having from 6 to 20 carbon atoms, and most preferred

is a cyano group.

Z^2 represents a hydrogen atom or a substituent and the substituent is an aliphatic group, an aromatic group or a heterocyclic group. Z^2 is preferably an aliphatic group, more preferably an alkyl group having from 1 to 6 carbon atoms.

Q represents a hydrogen atom or a substituent and the substituent is an aliphatic group, an aromatic group or a heterocyclic group. Q is preferably a group comprising a nonmetallic atom group necessary for forming a 5-, 6-, 7- or 8-membered ring. The 5-, 6-, 7- or 8-membered ring may be substituted, may be a saturated ring or may have an unsaturated bond. Q is more preferably an aromatic group or a heterocyclic group. Preferred examples of the nonmetallic atom include a nitrogen atom, an oxygen atom, a sulfur atom and a carbon atom. Specific examples of the ring structure include a benzene ring, a cyclopentane ring, a cyclohexane ring, a cycloheptane ring, a cyclooctane ring, a cyclohexene ring, a pyridine ring, a pyrimidine ring, a pyrazine ring, a pyridazine ring, a triazine ring, an imidazole ring, a benzimidazole ring, an oxazole ring, a benzoxazole ring, a thiazole ring, a benzothiazole ring, an oxane ring, a sulfolane ring and a thiane ring.

The hydrogen atom of each substituent described in regard to formula (1a) may be substituted. Examples of the

substituent include the substituents described in regard to formula (1), the groups described as examples for G, R^1 and R^2, and ionic hydrophilic groups.

Here, the Hammett's substituent constant σp value used in the present invention is described. The Hammett's rule is an empirical rule advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a σp value and a σm value and these values can be found in a large number of general publications but these are described in detail, for example, in J.A. Dean (compiler), Lange's Handbook of Chemistry, 12th ed., McGraw-Hill (1979), and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979). In the present invention, each substituent is limited or described by using the Hammett's substituent constant σp but this does not mean that the substituent is limited only to those having a known value which can be found in the above-described publications. Needless to say, the substituent includes substituents of which σp value is not known in publications but when measured based on the Hammett's rule, falls within the range specified. Furthermore, although formula (1a) of the present invention

includes those which are not a benzene derivative, the σp value is used as a measure for showing the electron effect of the substituent irrespective of the substitution site. In the present invention, the σp value is used in such a meaning.

Examples of the electron-withdrawing group having a Hammett's substituent constant σp value of 0.60 or more include a cyano group, a nitro group, an alkylsulfonyl group (e.g., methylsulfonyl) and an arylsulfonyl group (e.g., phenylsulfonyl).

Examples of the electron-withdrawing group having a Hammett's σp value of 0.45 or more include, in addition to those described above, an acyl group (e.g., acetyl), an alkoxycarbonyl group (e.g., dodecyloxycarbonyl), an aryloxycarbonyl group (e.g., m-chlorophenoxycarbonyl), an alkylsulfinyl group (e.g., n-propylsulfinyl), an aryl-sulfinyl group (e.g., phenylsulfinyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dimethylsulfamoyl) and a halogenated alkyl group (e.g., trifluoromethyl).

Examples of the electron-withdrawing group having a Hammett's substituent constant σp value of 0.30 or more include, in addition to those described above, an acyloxy group (e.g., acetoxy), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a halogenated alkoxy group (e.g., trifluoromethyloxy), a halogenated aryloxy

group (e.g., pentafluorophenyloxy), a sulfonyloxy group (e.g., methylsulfonyloxy), a halogenated alkylthio group (e.g., difluoromethylthio), an aryl group substituted by two or more electron-withdrawing groups having a σp value of 0.15 or more (e.g., 2,4-dinitrophenyl, pentachlorophenyl) and a heterocyclic ring (e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl).

Specific examples of the electron-withdrawing group having a σp value of 0.20 or more include, in addition to those described above, a halogen atom.

The preferred combination of substituents in the azo dye represented by formula (1) is described below. R^5 and R^6 each is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a sulfonyl group or an acyl group, more preferably a hydrogen atom, an aryl group, a heterocyclic group or a sulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group. However, R^5 and R^6 are not a hydrogen atom at the same time.

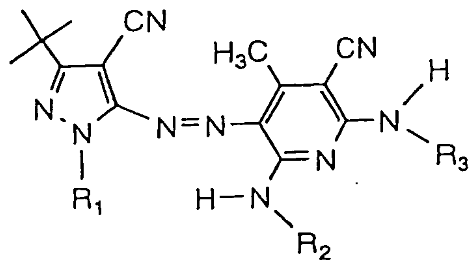
G is preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxyl group, an amino group or an acylamino group, more preferably a hydrogen atom, a halogen atom, an amino group or an acylamino group, and most preferably a hydrogen atom, an amino group or an acylamino group.

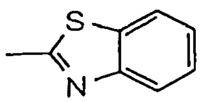
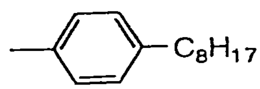
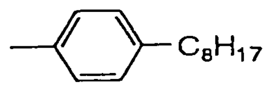
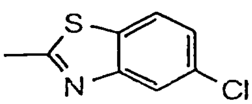
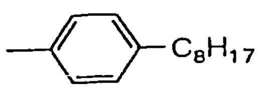
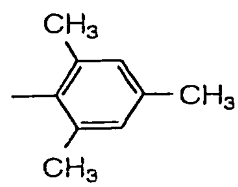
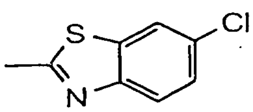
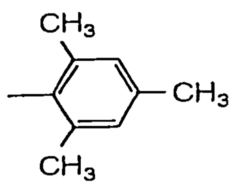
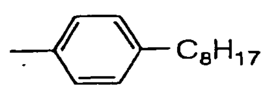
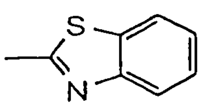
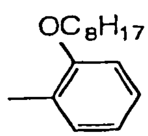
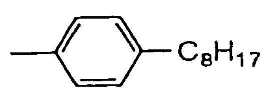
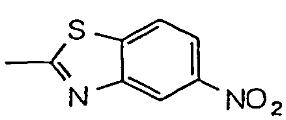
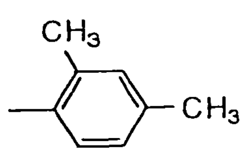
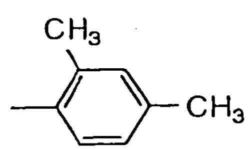
A is preferably a pyrazole ring, an imidazole ring, an isothiazole ring, a thiadiazole ring or a benzothiazole ring, more preferably a pyrazole ring or an isothiazole ring, and most preferably a pyrazole ring.

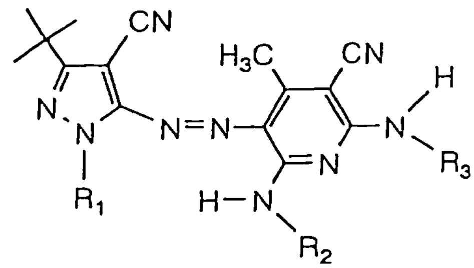
B^1 and B^2 each is $=CR^1-$ or $-CR^2=$, and R^1 and R^2 each is preferably a hydrogen atom, an alkyl group, a halogen atom, a cyano group, a carbamoyl group, a carboxyl group, a hydroxyl group, an alkoxy group or an alkoxycarbonyl group, more preferably a hydrogen atom, an alkyl group, a carboxyl group, a cyano group or a carbamoyl group.

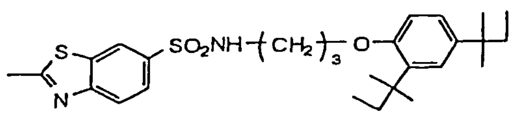
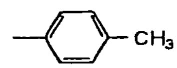
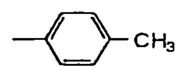
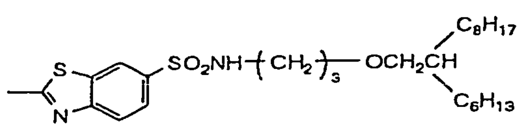
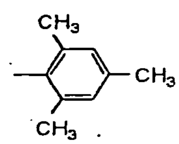
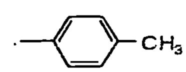
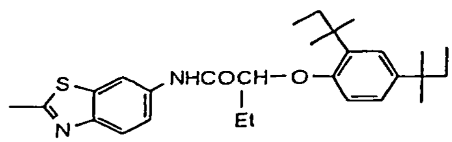
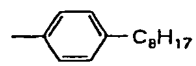
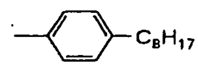
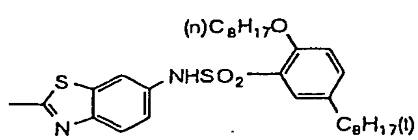
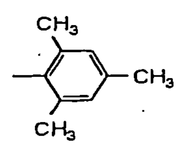
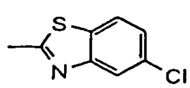
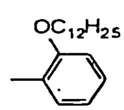
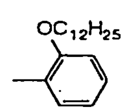
As for the preferred combination of substituents in the compound represented by formula (1), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

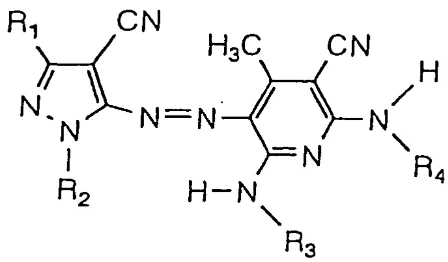
Specific examples of the azo dye represented by formula (1) are set forth below as Compounds a-1 to a-46, b-1 to b-8, c-1 to c-5, d-1 to d-5, e-1 to e-5, f-1 and f-2, but the azo dye for use in the present invention is not limited to these examples.

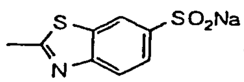
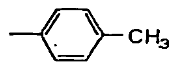
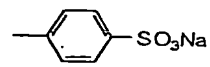
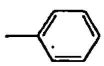
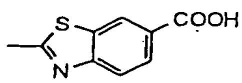
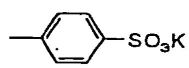
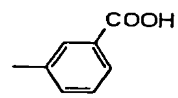
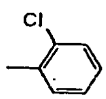
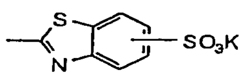
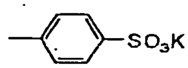
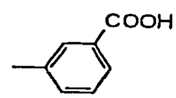
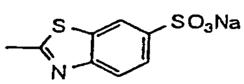
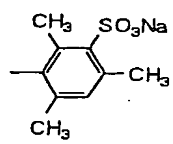
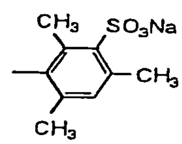
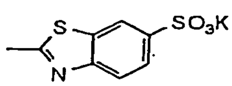
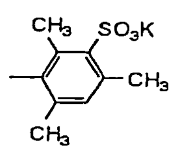
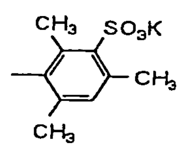
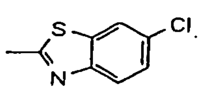
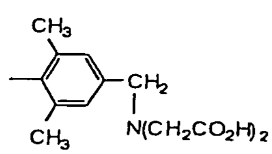
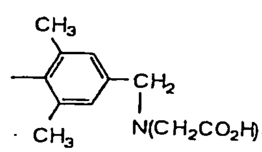
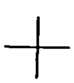
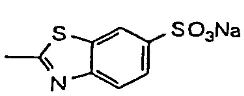
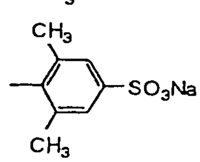
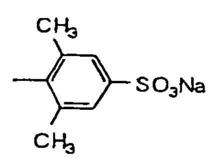


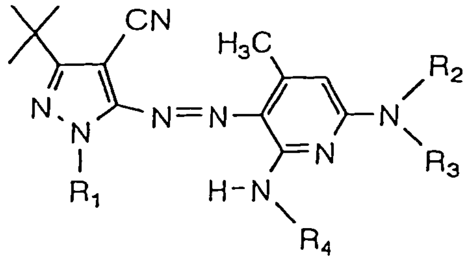
Dye	R_1	R_2	R_3
a−1			
a−2			
a−3			
a−4			
a−5			

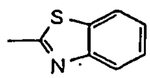
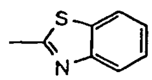
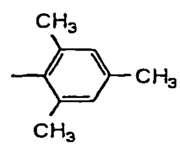
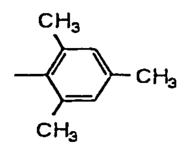
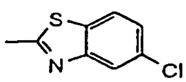
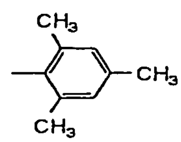
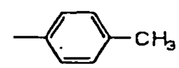
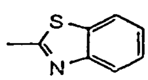
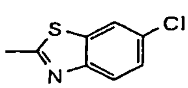
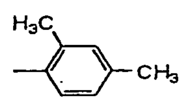
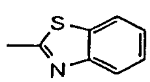
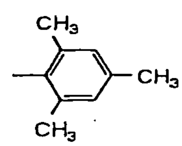
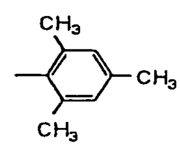
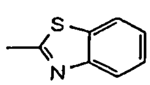
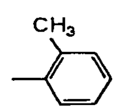
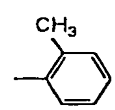
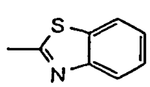
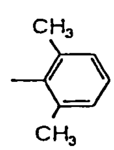
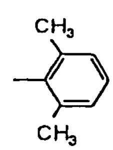
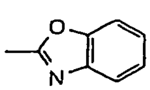
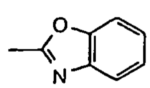
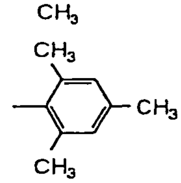
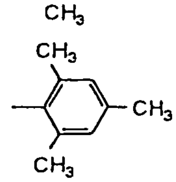


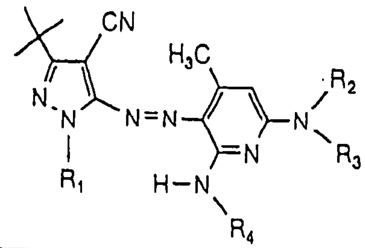
Dye	R_1	R_2	R_3
a-6			
a-7			
a-8			
a-9			$C_8H_{17}(t)$
a-10			

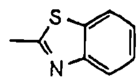
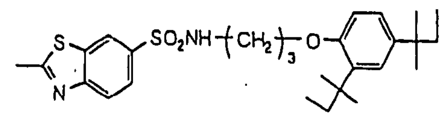
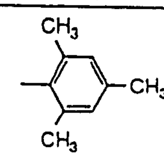
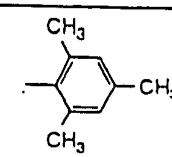
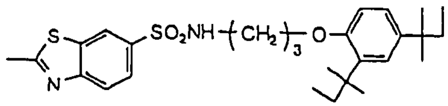
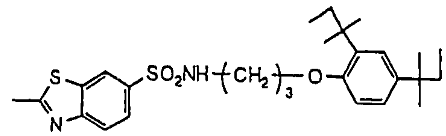
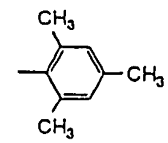
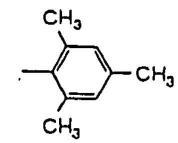
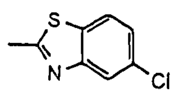
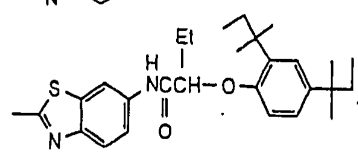
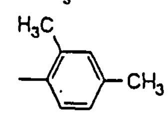
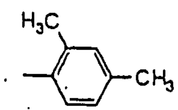
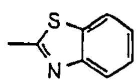
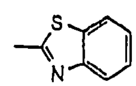
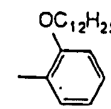
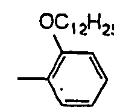
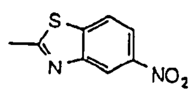
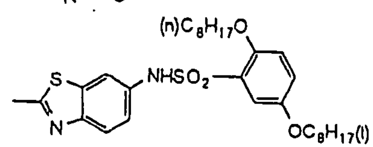
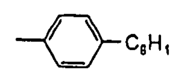
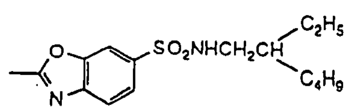
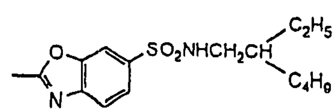
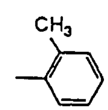
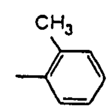


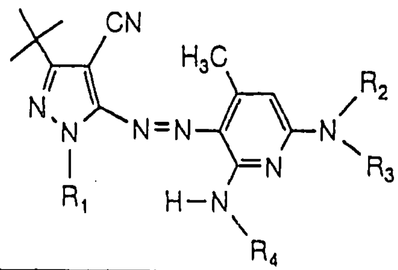
Dye	R_1	R_2	R_3	R_4
a-11				
a-12				
a-13		 (4,5-mix)		
a-14				
a-15				
a-16				
a-17				

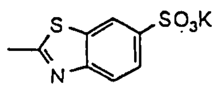
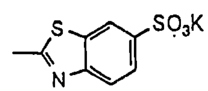
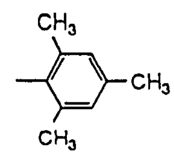
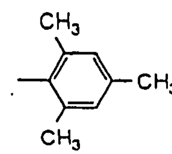
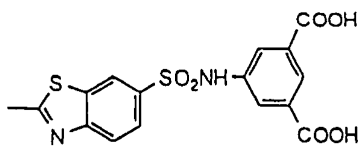
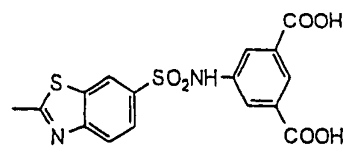
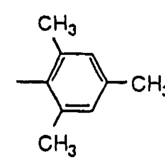
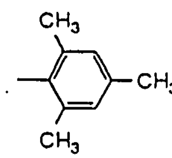
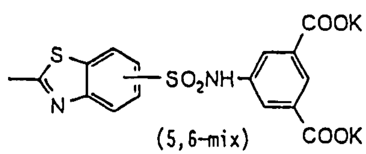
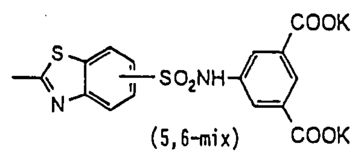
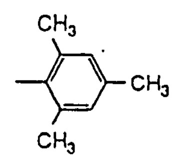
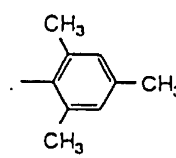
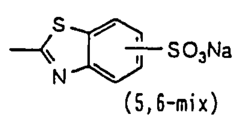
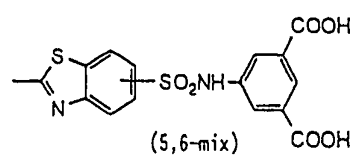
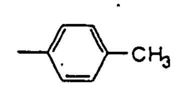
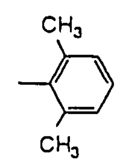


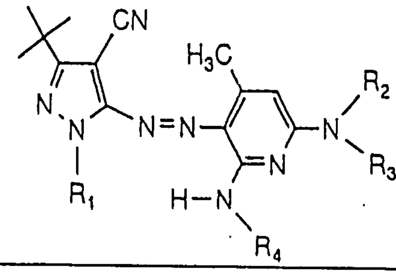
Dye	R_1	R_2	R_3	R_4
a−18				
a−19		$-SO_2CH_3$		
a−20		$-COCH_3$	$C_8H_{17}(t)$	$C_8H_{17}(t)$
a−21		$-SO_2CH_3$		$C_8H_{17}(t)$
a−22		H		
a−23		H		
a−24		H		
a−25				

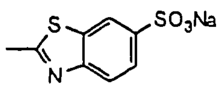
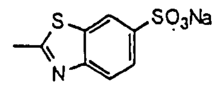
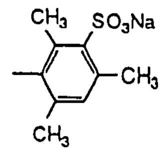
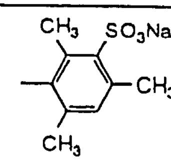
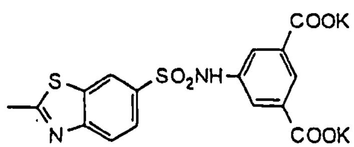
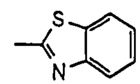
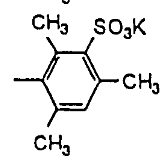
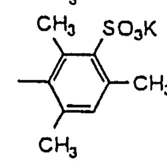
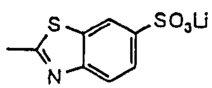
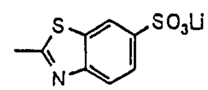
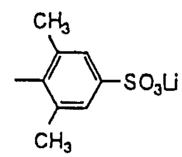
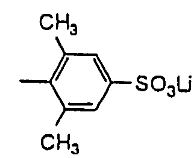
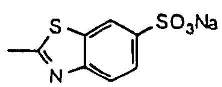
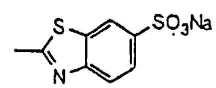
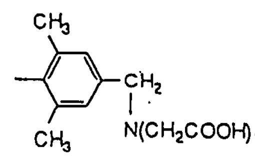
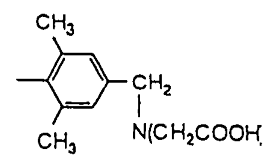
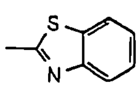
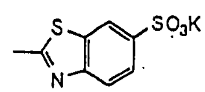
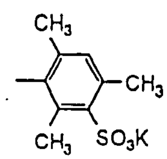
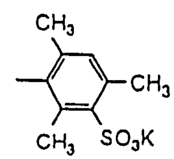


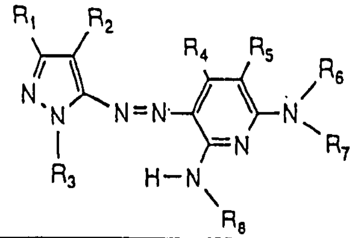
Dye	R_1	R_2	R_3	R_4
a-26				
a-27				
a-28				
a-29				
a-30				$C_8H_{17}(t)$
a-31				

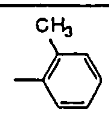
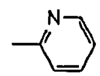
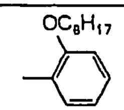
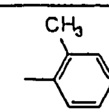
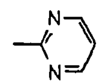
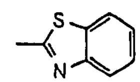
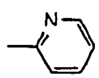
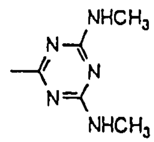
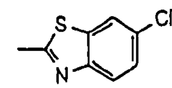
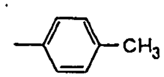
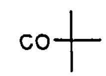
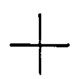
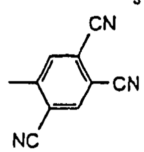
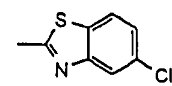
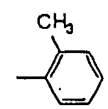
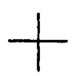
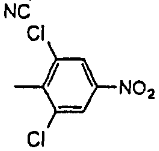
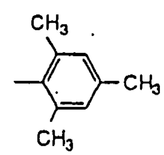
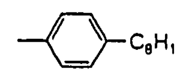
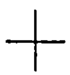
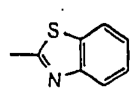
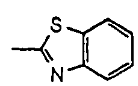
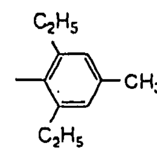
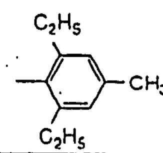


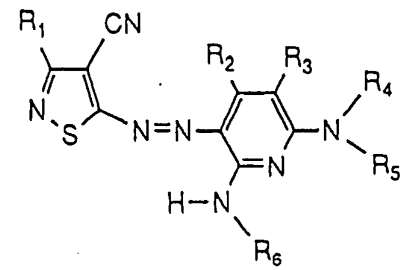
Dye	R_1	R_2	R_3	R_4
a-32				
a-33				
a-34				
a-35				

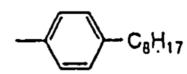
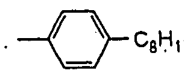
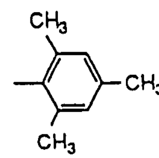
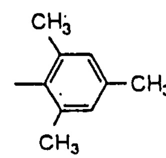
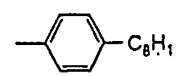
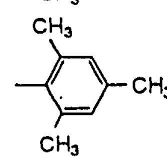
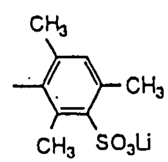
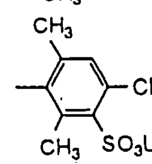
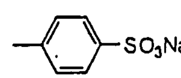
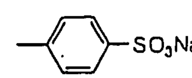


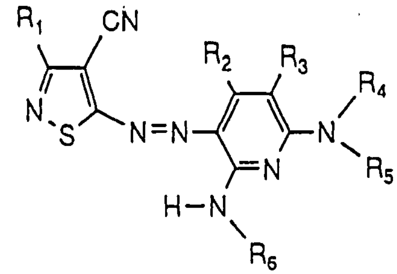
Dye	R_1	R_2	R_3	R_4
a-36				
a-37				
a-38				
a-39				
a-40				

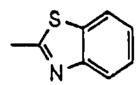
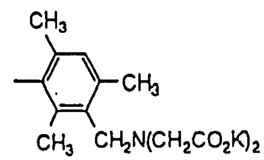
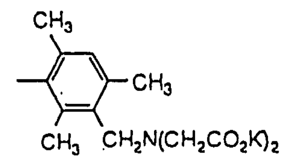
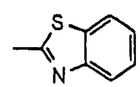
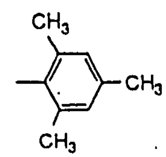
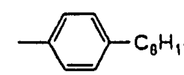
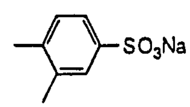
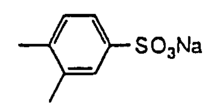


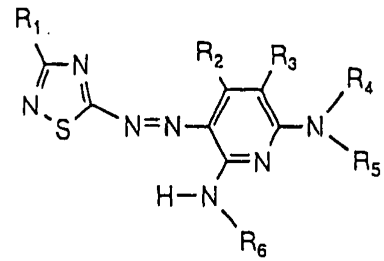
Dye	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
a-41		CN		H	$CONH_2$	SO_2CH_3		
a-42		Br		COOEt	H		$C_8H_{17}(t)$	$COCH_3$
a-43		SO_2CH_3		$CONH_2$	H			
a-44		CN		H	H			SO_2CH_3
a-45		Br		H	$CONH_2$	$\underset{\underset{O}{\|}}{C}CH_3$		
a-46		CN		CH_3	H			

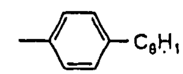
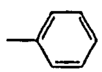
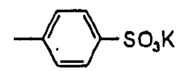
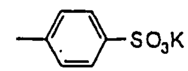
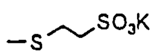
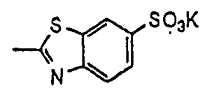
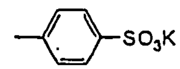
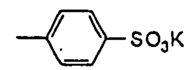
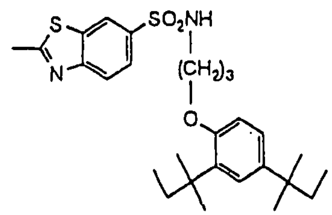
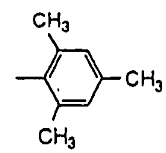
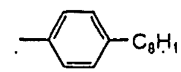
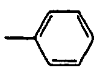
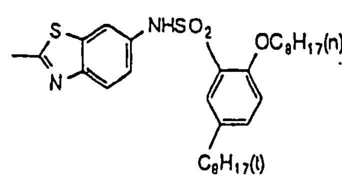
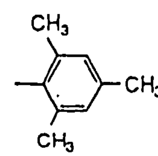


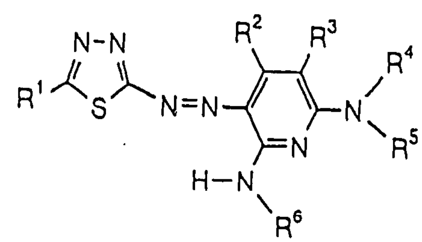
Dye	R_1	R_2	R_3	R_4	R_5	R_6
b-1	CH_3	CH_3	CN	H		
b-2	CH_3	CH_3	CN	H		
b-3	CH_3	CH_3	$CONH_2$	H		
b-4	CH_3	CH_3	H	H		
b-5	CH_3	H	CN	H		

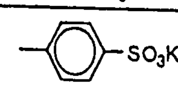
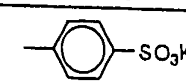
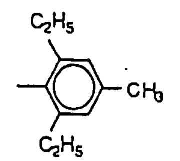
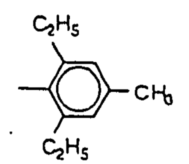
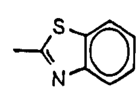
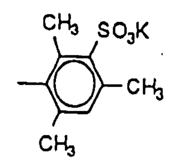
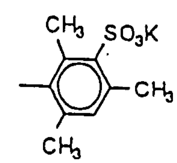
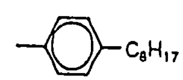
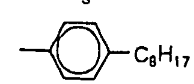
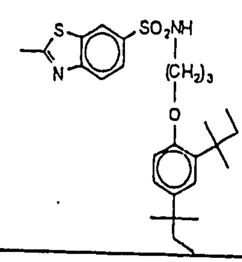
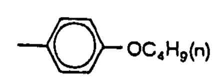
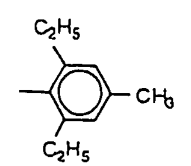


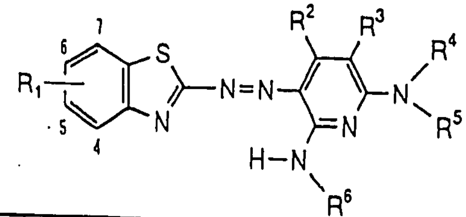
Dye	R_1	R_2	R_3	R_4	R_5	R_6
b-6	CH_3	CH_3	H			
b-7	CH_3	CH_3	H			
b-8	CH_3	H	H	SO_2CH_3		

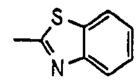
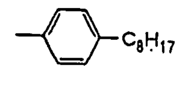
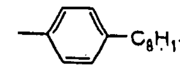
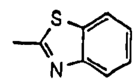
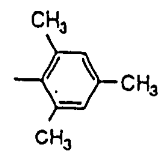
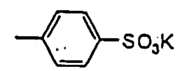
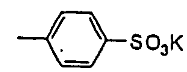
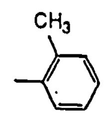
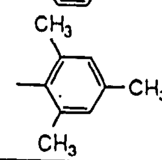


Dye	R_1	R_2	R_3	R_4	R_5	R_6
c-1	$-SCH_3$	CH_3	CN	H	$C_8H_{17}(t)$	
c-2		H	$CONH_2$	H		
c-3		CH_3	H			
c-4	$-CH_3$	CH_3	H			
c-5		H	H			$C_8H_{17}(t)$

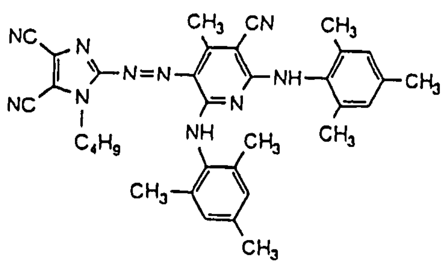


Dye	R_1	R_2	R_3	R_4	R_5	R_6
d-1	Me	CH_3	CN	H		
d-2	Me	CH_3	CN	H		
d-3	Me	H	H			
d-4	Ph	CH_3	$CONH_2$	H		
d-5	Ph	CH_3	H			

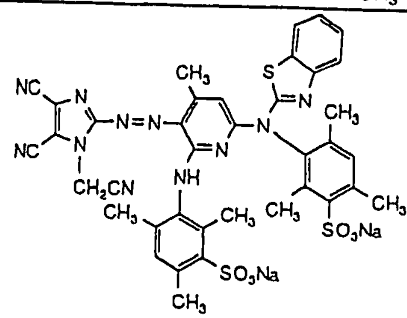


Dye	R_1	R_2	R_3	R_4	R_5	R_6
e-1	5-Cl	CH_3	$CONH_2$	H	$C_8H_{17}(t)$	$C_8H_{17}(t)$
e-2	5,6-diCl	H	H			
e-3	5,6-diCl	CH_3	H			$COCH_3$
e-4	5-CH_3	H	CN	H		
e-5	5-NO_2	CH_3	H	SO_2CH_3		

f-1



f-2



The inkjet recording magenta ink for use in the present invention has a main absorption region of 500 to 580 nm and is preferably obtained by dissolving or dispersing at least one of the above-described azo dyes in an aqueous medium. In this case, the azo dye is preferably contained in an amount of 0.2 to 20 weight %, more preferably from 0.5 to 15 weight %, and the solubility in water at 20°C (or dispersion degree in a stable state) is preferably 5 weight % or more, more preferably 10 weight % or more.

The dye of formula (1), which is particularly preferred as the colorant constituting the magenta ink for use in the present invention, is substantially water-soluble or water-dispersible, more specifically, the solubility of the colorant in water at 20°C is preferably 2 weight % or more, more preferably 5 weight % or more.

In preparing an ink set comprising two or more inks sharing the main absorption region, generally, one ink is produced as a light-type thin ink and another is produced as a thick ink. In this case, the absorbance of light ink and the absorbance of dark ink are in the above-described relationship.

The dye contained in each constituent ink may be a single dye or a mixture of dyes, but in either case, at least one ink is preferably prepared by dissolving or

dispersing at least one dye represented by formula (1) in an aqueous medium to a concentration of 0.2 to 20 weight %, more preferably from 0.5 to 15 weight %.

The dye represented by formula (1) may be used alone, but in the case of using the dye in combination with other colorants, the colorant combined may be either a dye or a pigment and may be in the form of being dissolved in an aqueous medium or in the form that a pigment insoluble in the aqueous medium is present in the dispersed state. In the case of a pigment, the solubility (at 25°C) in water is 0.1 g/100 g or less in many cases. As for the ink composition where the component is dispersed, examples of the component include an emulsion dispersion, a polymer dye, a dye supported on or dispersed in a polymer, and a pigment. Among these, a pigment is preferred.

Also, the dye ink may contain a water-insoluble pigment in the dispersed state or the pigment ink may contain a water-soluble dye.

When a dye represented by formula (1) and a different dye or a pigment are present in combination in one ink composition, the total concentration thereof is from 0.2 to 20 weight %, preferably from 0.5 to 15 weight %.

The magenta dye having an azo group for use in the present invention has an oxidation potential, in an aqueous medium for ink, of more positive than 0.7 V vs SCE,

preferably more positive than 0.8 V vs SCE, more preferably more positive than 1.0 V vs SCE. The potential can be elevated by selecting the preferred structural features described above, more specifically, by selecting a dye structure of the type having a chromophore represented by (heterocyclic ring A)-N=N-(heterocyclic ring B), selecting an azo dye in which an aromatic nitrogen-containing 6-membered heterocyclic ring is bonded as a coupling component directly to at least one side of the azo group, and selecting an azo dye having an aromatic ring amino group- or heterocyclic amino group-containing structure as an auxochrome, and furthermore by removing α hydrogen of the azo dye. In particular, the dye of formula (1) expresses a positive potential. This is specifically described in Japanese Patent Application No. 2001-254878.

The oxidation potential value (Eox) can be easily measured by one skilled in the art and the method therefor is described, for example, in P. Delahay, <u>New Instrumental Methods in Electrochemistry</u>, Interscience Publishers (1954), A.J. Bard et al., <u>Electrochemical Methods</u>, John Wiley & Sons (1980), and Akira Fujishima et al., <u>Denkikagaku Sokutei Ho (Electrochemical Measuring Method)</u>, Gihodo Shuppan Sha (1984).

More specifically, the oxidation potential can be measured by various measuring methods such as direct

current polarography which is a method of measuring the oxidation potential in an aqueous solution or water-mixed solvent system having dissolved therein the dye based on SCE (standard saturated calomel electrode) as the reference electrode and in which a graphite electrode and a platinum electrode are used as the working electrode and the counter electrode, respectively; polarography in which a dropping mercury electrode is used; cyclic voltammetry method (CV); rotating ring-disk electrode method; and comb electrode method. The oxidation potential is measured as follows. A test sample is dissolved to a concentration of 1×10^{-4} to 1×10^{-6} $mol\cdot dm^{-3}$ in a solvent such as dimethylformamide or acetonitrile containing a supporting electrolyte such as sodium perchlorate or tetrapropylammonium perchlorate and the oxidation potential is measured as a value to SCE (standard saturated calomel electrode) by using the above-described method. The supporting electrolyte and solvent used can be appropriately selected according to the oxidation potential or solubility of the test sample. The supporting electrolyte and solvent which can be used are described in Akira Fujishima et al., Denkikagaku Sokutei Ho (Electrochemical Measuring Method), pp. 101-118, Gihodo Shuppan Sha (1984).

The oxidation potential value sometimes deviates on the order of several tens of millivolts due to the effect

of, for example, liquid junction potential or liquid resistance of the sample solution, but the reproducibility of measured potential value can be guaranteed by the calibration using a standard sample (for example, hydroquinone) and the same measured value can be obtained by any of those potential measuring methods.

<Colorants Sharing Main Absorption Region of 580 to 600 nm>

The colorant of the cyan ink set excellent in the fastness and pictorial quality, which is combined with the magenta ink set for forming a full color image, is described below. The colorants contained in the cyan ink set for inkjet recording of the present invention are colorants sharing the main absorption region of 580 to 600 nm. At least one constituent colorant is preferably a phthalocyanine dye represented by formula (I).

The phthalocyanine dye is a dye having fastness but this dye is known to be inferior in the fastness to ozone gas when used as a dye for inkjet recording. In the phthalocyanine dye represented by formula (I), this defect is overcome by its chemical structure.

In the phthalocyanine dye represented by formula (I), an electron-withdrawing group is introduced into the phthalocyanine skeleton so as to reduce the reactivity with ozone which is an electrophilic agent. The oxidation potential of this dye is more positive than 0.7 V (vs SCE)

in many cases. A more positive oxidation potential is more preferred and the oxidation potential is more preferably more positive than 1.0 V (vs SCE) and most preferably more positive than 1.2 V (vs SCE).

The oxidation potential (sometimes also referred to as "Eox") value indicates the transferability of an electron from the sample to the electrode and as the value is larger (the oxidation potential is positivef), the electron is less transferable from the sample to the electrode, in other words, the oxidation less occurs. As for the relationship with the structure of compound, the oxidation potential becomes more positive when an electron-withdrawing group is introduced, and becomes baser when an electron-donating group is introduced. In the present invention, the oxidation potential is preferably rendered more positive by introducing an electron-withdrawing group into the phthalocyanine skeleton so as to reduce the reactivity with ozone which is an electrophilic agent. When the Hammett's substituent constant σp value as a measure for the electron-withdrawing property or electron-donating property of substituent is used, the oxidation potential can be rendered more positive by introducing a substituent having a large σp value, such as sulfinyl group, sulfonyl group and sulfamoyl group.

Also from the standpoint of such potential control,

the phthalocyanine dye represented by formula (I) is preferably used.

The oxidation potential of the phthalocyanine dye is measured by commonly employed methods described above regarding the magenta ink set.

In formula (I), X_1, X_2, X_3 and X_4 each independently represents $-SO-Z$, $-SO_2-Z$, $-SO_2NR_1R_2$, a sulfo group, $-CONR_1R_2$ or $-CO_2R_1$. Among these substituents, preferred are $-SO-Z$, $-SO_2-Z$, $-SO_2NR_1R_2$ and $-CONR_1R_2$, more preferred are $-SO_2-Z$ and $-SO_2NR_1R_2$, and most preferred is $-SO_2-Z$. In the case where a_1 to a_4 showing the number of substituents each represents a number of 2 or more, multiple substituents X_1, X_2, X_3 or X_4 may be the same or different and each independently represents any one of the above-described groups. X_1, X_2, X_3 and X_4 may be completely the same substituents, may be substituents of the same kind but partially different as in the case, for example, where X_1, X_2, X_3 and X_4 all are $-SO_2-Z$ and Zs are different from each other, or may contain substituents different from each other, for example, $-SO_2-Z$ and $-SO_2NR_1R_2$.

Each Z independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted

or unsubstituted heterocyclic group, preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group.

R_1 and R_2 each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, preferably a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, more preferably a hydrogen atom, a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. However, it is not preferred that R_1 and R_2 both are a hydrogen atom.

The substituted or unsubstituted alkyl group represented by R_1, R_2 and Z is preferably an alkyl group having from 1 to 30 carbon atoms, more preferably a branched alkyl group because the solubility of dye and the stability of ink are improved, still more preferably an alkyl group having an asymmetric carbon (use in the racemic

form). Examples of the substituent include those described later as the substituent when Z, R_1, R_2, Y_1, Y_2, Y_3 and Y_4 can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the alkyl group may be substituted by a halogen atom or an ionic hydrophilic group. Incidentally, the number of carbon atoms in the alkyl group does not include carbon atoms of substituents and this applies to other groups.

The substituted or unsubstituted cycloalkyl group represented by R_1, R_2 and Z is preferably a cycloalkyl group having from 5 to 30 carbon atoms, more preferably a cycloalkyl group having an asymmetric carbon (use in the racemic form) because the solubility of dye and the stability of ink are improved. Examples of the substituent include those described later as the substituent when Z, R_1, R_2, Y_1, Y_2, Y_3 and Y_4 can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the cycloalkyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted alkenyl group represented by R_1, R_2 and Z is preferably an alkenyl group having from 2 to 30 carbon atoms, more preferably a branched alkenyl group because the solubility of dye and the stability of ink are improved, still more preferably an alkenyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when Z, R_1, R_2, Y_1, Y_2, Y_3 and Y_4 can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the alkenyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted aralkyl group represented by R_1, R_2 and Z is preferably an aralkyl group having from 7 to 30 carbon atoms, more preferably a branched aralkyl group because the solubility of dye and the stability of ink are improved, still more preferably an aralkyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when Z, R_1, R_2, Y_1, Y_2, Y_3 and Y_4 can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred

because the aggregating property and fastness of dye are enhanced. Other than these, the aralkyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted aryl group represented by R_1, R_2 and Z is preferably an aryl group having from 6 to 30 carbon atoms. Examples of the substituent include those described later as the substituent when Z, R_1, R_2, Y_1, Y_2, Y_3 and Y_4 can further have a substituent. In particular, an electron-withdrawing group is preferred because the dye can have a positive oxidation potential and can be improved in the fastness. Examples of the electron-withdrawing group include those having a positive Hammett's substituent constant σp value. Among these, preferred are a halogen atom, a heterocyclic group, a cyano group, a carboxyl group, an acylamino group, a sulfonamido group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imido group, an acyl group, a sulfo group and a quaternary ammonium group, more preferred are a cyano group, a carboxyl group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imido group, an acyl group, a sulfo group and a quaternary ammonium group.

The heterocyclic group represented by R_1, R_2 and Z is preferably a 5- or 6-membered ring and the ring may be further condensed and may be an aromatic heterocyclic group or a non-aromatic heterocyclic group. Examples of the

heterocyclic group represented by R_1, R_2 and Z are shown below in the form of a heterocyclic ring by omitting the substitution site. The substitution site is not limited and, for example, in the case of pyridine, the 2-position, 3-position and 4-position can be substituted. Examples include pyridine, pyrazine, pyrimidine, pyridazine, triazine, quinoline, isoquinoline, quinazoline, cinnoline, phthalazine, quinoxaline, pyrrole, indole, furan, benzofuran, thiophene, benzothiophene, pyrazole, imidazole, benzimidazole, triazole, oxazole, benzoxazole, thiazole, benzothiazole, isothiazole, benzisothiazole, thiadiazole, isoxazole, benzisoxazole, pyrrolidine, piperidine, piperazine, imidazolidine and thiazoline. In particular, an aromatic heterocyclic group is preferred. Preferred examples thereof include, shown in the same manner as above, pyridine, pyrazine, pyrimidine, pyridazine, triazine, pyrazole, imidazole, benzimidazole, triazole, thiazole, benzothiazole, isothiazole, benzisothiazole and thiadiazole. These groups each may have a substituent and examples of the substituent include those described later as the substituent when Z, R_1, R_2, Y_1, Y_2, Y_3 and Y_4 can further have a substituent. Preferred substituents are the same as the substituents of the above-described aryl group and more preferred substituents are the same as the more preferred substituents of the above-described aryl group.

Y_1, Y_2, Y_3 and Y_4 each independently represents a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, an amino group, an alkylamino group, an alkoxy group, an aryloxy group, an acylamino group, an arylamino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxycarbonyl group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonyl group, an aryloxycarbonylamino group, an imido group, a heterocyclic thio group, a phosphoryl group, an acyl group, a carboxyl group or a sulfo group. These groups each may further have a substituent.

Y_1, Y_2, Y_3 and Y_4 each is preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amido group, a ureido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonyl group, a carboxyl group or a sulfo group, more preferably a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or a sulfo group, and most preferably a hydrogen atom.

When Z, R_1, R_2, Y_1, Y_2, Y_3 and Y_4 each is a group which

can further have a substituent, the group may further have a substituent described below.

Examples of the substituent include a linear or branched alkyl group having from 1 to 12 carbon atoms, a linear or branched aralkyl group having from 7 to 18 carbon atoms, a linear or branched alkenyl group having from 2 to 12 carbon atoms, a linear or branched alkynyl group having from 2 to 12 carbon atoms, a linear or branched cycloalkyl group having from 3 to 12 carbon atoms, a linear or branched cycloalkenyl group having from 3 to 12 carbon atoms (these groups each is preferably a group having a branched chain because the solubility of dye and the stability of ink are improved, more preferably a group having an asymmetric carbon; specific examples of the groups include methyl, ethyl, propyl, isopropyl, sec-butyl, tert-butyl, 2-ethylhexyl, 2-methylsulfonylethyl, 3-phenoxypropyl, trifluoromethyl and cyclopentyl), a halogen atom (e.g., chlorine, bromine), an aryl group (e.g., phenyl, 4-tert-butylphenyl, 2,4-di-tert-amylphenyl), a heterocyclic group (e.g., imidazolyl, pyrazolyl, triazolyl, 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl), a cyano group, a hydroxyl group, a nitro group, a carboxy group, an amino group, an alkyloxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-methanesulfonylethoxy), an aryloxy group (e.g., phenoxy, 2-methylphenoxy, 4-tert-butylphenoxy, 3-

nitrophenoxy, 3-tert-butyloxycarbamoylphenoxy, 3-methoxycarbamoyl), an acylamino group (e.g., acetamido, benzamido, 4-(3-tert-butyl-4-hydroxyphenoxy)butanamido), an alkylamino group (e.g., methylamino, butylamino, diethylamino, methylbutylamino), an anilino group (e.g., phenylamino, 2-chloroanilino), a ureido group (e.g., phenylureido, methylureido, N,N-dibutylureido), a sulfamoylamino group (e.g., N,N-dipropylsulfamoylamino), an alkylthio group (e.g., methylthio, octylthio, 2-phenoxyethylthio), an arylthio group (e.g., phenylthio, 2-butoxy-5-tert-octylphenylthio, 2-carboxyphenylthio), an alkyloxycarbonylamino group (e.g., methoxycarbonylamino), a sulfonamido group (e.g., methanesulfonamido, benzene-sulfonamido, p-toluenesulfonamido), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-phenylsulfamoyl), a sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, toluenesulfonyl), an alkyloxycarbonyl group (e.g., methoxycarbonyl, butyloxy-carbonyl), a heterocyclic oxy group (e.g., 1-phenyltetrazol-5-oxy, 2-tetrahydropyranyloxy), an azo group (e.g., phenylazo, 4-methoxyphenylazo, 4-pivaloylamino-phenylazo, 2-hydroxy-4-propanoylphenylazo), an acyloxy group (e.g., acetoxy), a carbamoyloxy group (e.g., N-methylcarbamoyloxy, N-phenylcarbamoyloxy), a silyloxy group

(e.g., trimethylsilyloxy, dibutylmethylsilyloxy), an aryloxycarbonylamino group (e.g., phenoxycarbonylamino), an imido group (e.g., N-succinimido, N-phthalimido), a heterocyclic thio group (e.g., 2-benzothiazolylthio, 2,4-di-phenoxy-1,3,5-triazole-6-thio, 2-pyridylthio), a sulfinyl group (e.g., 3-phenoxypropylsulfinyl), a phosphonyl group (e.g., phenoxyphosphonyl, octyloxy-phosphonyl, phenylphosphonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), an acyl group (e.g., acetyl, 3-phenylpropanoyl, benzoyl), and an ionic hydrophilic group (e.g., carboxyl, sulfo, phosphono, quaternary ammonium).

In the case where the phthalocyanine dye represented by formula (I) is water-soluble, the dye preferably contains an ionic hydrophilic group. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetra-methylphosphonium). Among these counter ions, alkali metal

salts are preferred and a lithium salt is more preferred because the solubility of dye and the stability of ink are enhanced.

As for the number of ionic hydrophilic groups, the phthalocyanine dye preferably contains at least two ionic hydrophilic groups, more preferably at least two sulfo groups and/or carboxyl groups, within one molecule.

a_1 to a_4 and b_1 to b_4 represent the number of substituents X_1 to X_4 and Y_1 to Y_4, respectively. a_1 to a_4 each independently represents an integer of 0 to 4 but all are not 0 at the same time. b_1 to b_4 each independently represents an integer of 0 to 4. When a_1, a_2, a_3, a_4, b_1, b_2, b_3 or b_4 represents an integer of 2 or more, multiple X_1s, X_2s, X_3s, X_4s, Y_1s, Y_2s, Y_3s or Y_4s are present and these may be the same or different.

a_1 and b_1 satisfy the relationship of $a_1+b_1=4$. In particular, a combination that a_1 represents 1 or 2 and b_1 represents 3 or 2 is preferred, and a combination that a_1 represents 1 and b_1 represents 3 is most preferred.

The same relationship as that between a_1 and b_1 is present in each of pairs a_2 and b_2, a_3 and b_3, and a_4 and b_4, and the preferred combination is also the same.

M represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof.

M is preferably a hydrogen atom, a metal element such

as Li, Na, K, Mg, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Si, Ge, Sn, Pb, Sb and Bi, an oxide such as VO and GeO, a hydroxide such as $Si(OH)_2$, $Cr(OH)_2$ and $Sn(OH)_2$, or a halide such as AlCl, $SiCl_2$, VCl, VCl_2, VOCl, FeCl, GaCl and ZrCl, more preferably Cu, Ni, Zn or Al, and most preferably Cu.

Also, Pc (phthalocyanine ring) may form a dimer (for example, Pc-M-L-M-Pc) or a trimer through L (divalent linking group). At this time, Ms may be the same or different.

The divalent linking group represented by L is preferably an oxy group -O-, a thio group -S-, a carbonyl group -CO-, a sulfonyl group $-SO_2-$, an imino group -NH-, a methylene group $-CH_2-$ or a group formed by combining two or more of these groups.

As for the preferred combination of substituents in the compound represented by formula (I), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

Among the phthalocyanine dyes represented by formula (I), a phthalocyanine dye having a structure represented by

formula (II) is preferred. The phthalocyanine dye represented by formula (II) of the present invention is described in detail below.

In formula (II), X_{11} to X_{14} and Y_{11} to Y_{18} have the same meanings as X_1 to X_4 and Y_1 to Y_4 in formula (I), respectively, and preferred examples are also the same. M has the same meaning as M in formula (I) and preferred examples are also the same.

In formula (II), a_{11} to a_{14} each independently represents an integer of 1 or 2 and preferably satisfy $4 \le a_{11}+a_{12}+a_{13}+a_{14} \le 6$, and $a_{11}=a_{12}=a_{13}=a_{14}=1$ is more preferred.

X_{11}, X_{12}, X_{13} and X_{14} may be completely the same substituents, may be substituents of the same kind but partially different as in the case, for example, where X_{11}, X_{12}, X_{13} and X_{14} all are $-SO_2-Z$ and Zs are different from each other, or may contain substituents different from each other, for example, $-SO_2-Z$ and $-SO_2NR_1R_2$.

In the phthalocyanine dye represented by formula (II), the following combinations of substituents are particularly preferred.

X_{11} to X_{14} each independently represents preferably $-SO-Z$, $-SO_2-Z$, $-SO_2NR_1R_2$ or $-CONR_1R_2$, more preferably $-SO_2-Z$ or $-SO_2NR_1R_2$, and most preferably $-SO_2-Z$.

Each Z independently represents preferably a substituted or unsubstituted alkyl group, a substituted or

unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. In particular, the case where an asymmetric carbon is present in the substituent (use in the racemic form) is preferred because the solubility of dye and the stability of ink are enhanced. Also, the case where a hydroxyl group, an ether group, an ester group, a cyano group, an amido group or a sulfonamido group is present in the substituent is preferred because the aggregating property and fastness are improved.

R_1 and R_2 each independently represents preferably a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, more preferably a hydrogen atom, a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. However, it is not preferred that R_1 and R_2 both are a hydrogen atom. In particular, the case where an asymmetric carbon is present in the substituent (use in the racemic form) is preferred because the solubility of dye and the stability of ink are enhanced. Also, the case where a hydroxyl group, an ether group, an ester group, a cyano group, an amido group or a sulfonamido group is present in the substituent is preferred because the aggregating property and fastness

are improved.

Y_{11} to Y_{18} each independently represents preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amido group, a ureido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonyl group, a carboxyl group or a sulfo group, more preferably a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or a sulfo group, and most preferably a hydrogen atom.

a_{11} to a_{14} each independently represents preferably 1 or 2 and it is more preferred that all are 1.

M represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof, preferably Cu, Ni, Zn or Al, and most preferably Cu.

In the case where the phthalocyanine dye represented by formula (II) is water-soluble, the dye preferably contains an ionic hydrophilic group. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium

ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these counter ions, alkali metal salts are preferred and a lithium salt is more preferred because the solubility of dye and the stability of ink are enhanced.

As for the number of ionic hydrophilic groups, the phthalocyanine dye preferably contains at least two ionic hydrophilic groups, more preferably at least two sulfo groups and/or carboxyl groups, within one molecule.

As for the preferred combination of substituents in the compound represented by formula (II), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

As for the chemical structure of the phthalocyanine dye of the present invention, at least one electron-withdrawing group such as sulfinyl group, sulfonyl group and sulfamoyl group is preferably introduced into respective four benzene rings of phthalocyanine such that the total of σp values of the substituents in the entire phthalocyanine skeleton becomes 1.6 or more.

The Hammett's substituent constant σp value is

briefly described here. The Hammett's rule is an empirical rule advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a σp value and a σm value and these values can be found in a large number of general publications but these are described in detail, for example, in J.A. Dean (compiler), Lange's Handbook of Chemistry, 12th ed., McGraw-Hill (1979), and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979).

Inevitably in view of the synthesis method, the phthalocyanine derivative represented by formula (I) is generally a mixture of analogues differing in the sites where the substituents Xn (n=1 to 4) and Ym (m=1 to 4) are introduced and in the number of the substituents introduced. Accordingly, these analogue mixtures are statistically averaged and represented by a formula in many cases. In the present invention, it has been found that when these analogue mixtures are classified into the following three types, a specific mixture is particularly preferred. The phthalocyanine-base dye analogue mixtures represented by formulae (I) and (II) are defined by classifying these into the following three types based on the substitution site.

(1) β-Position substitution type:

A phthalocyanine dye having specific substituents at the 2- and/or 3-position, the 6- and/or 7-position, the 10- and/or 11-position, and the 14- and/or 15-position.

(2) α-Position substitution type:

A phthalocyanine dye having specific substituents at the 1- and/or 4-position, the 5- and/or 8-position, the 9- and/or 12-position, and the 13- and/or 16-position.

(3) α,β-Position mixed substitution type:

A phthalocyanine dye having specific substitutions at the 1- to 16-positions without any regularity.

In the present invention, phthalocyanine dye derivatives differing in the structure (particularly in the substitution site) are described by using these β-position substitution type, α-position substitution type and α,β-position mixed substitution type.

The phthalocyanine derivative for use in the present invention can be synthesized by combining the methods described or cited, for example, in Shirai and Kobayashi, <u>Phthalocyanine -Kagaku to Kino- (Phthalocyanine -Chemistry and Function-)</u>, pp. 1-62, IPC, and C.C. Leznoff and A.B.P. Lever, <u>Phthalocyanines - Properties and Applications</u>, pp. 1-54, VCH, or methods analogous thereto.

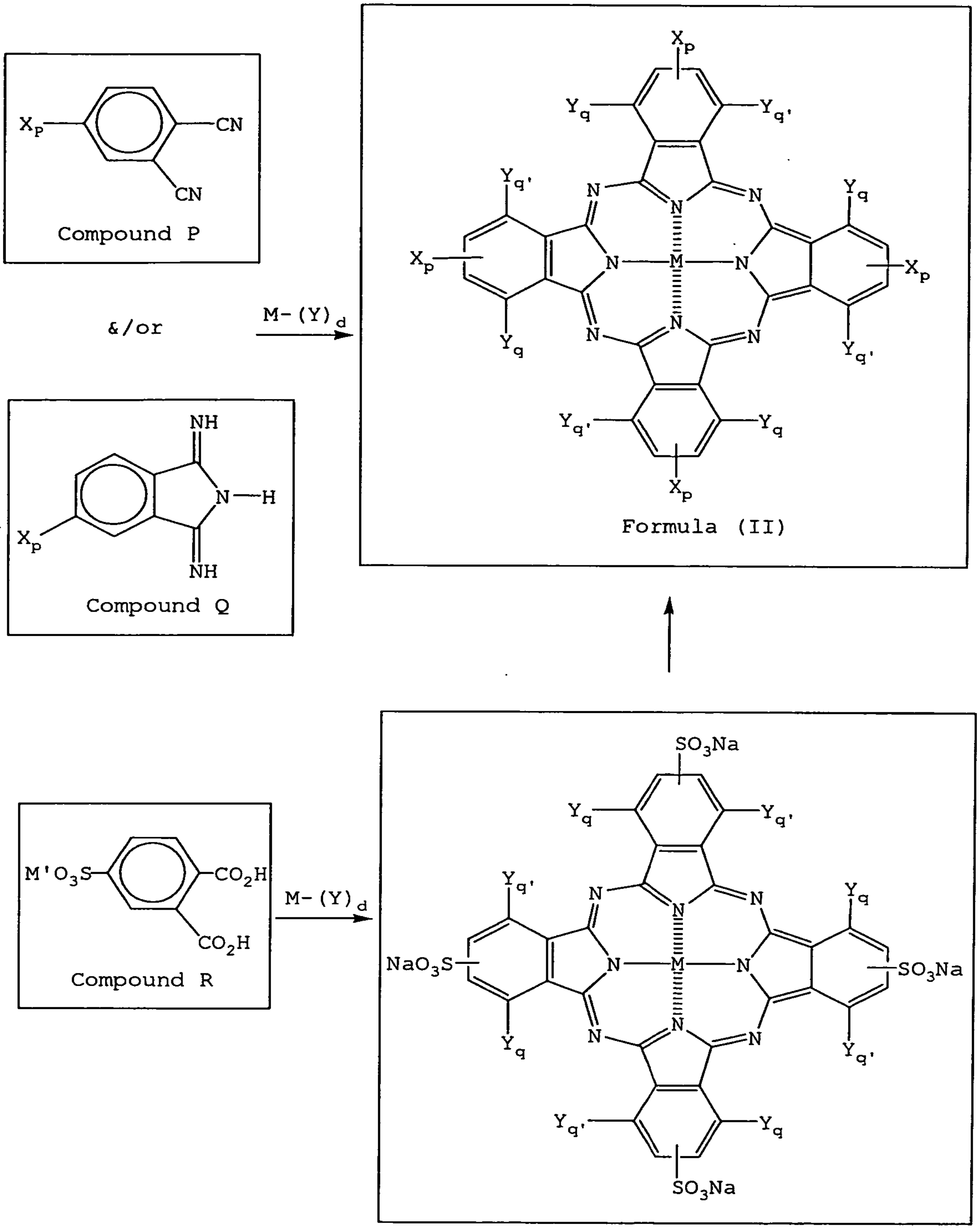
The phthalocyanine compound represented by formula (I) of the present invention can be synthesized, for

example, through sulfonation, sulfonyl chloridation or amidation reaction of an unsubstituted phthalocyanine compound as described in International Publications 00/17275, 00/08103, 00/08101 and 98/41853 and JP-A-10-36471. In this case, sulfonation may take place at any site of the phthalocyanine nucleus and the number of sites sulfonated is difficult to control. Accordingly, when a sulfo group is introduced under such reaction conditions, the positions and number of sulfo groups introduced into the product cannot be specified and a mixture of those differing in the number of substituents or in the substitution site inevitably results. If the compound of the present invention is synthesized starting from such a product, the compound of the present invention is obtained as an α,β-position mixed substitution type mixture containing several kinds of compounds differing in the number of substituents or in the substitution site, because the number of sulfamoyl groups substituted on the heterocyclic ring or their substitution sites cannot be specified.

As described above, for example, when many electron-withdrawing groups such as sulfamoyl group are introduced into the phthalocyanine nucleus, the oxidation potential becomes more positive and the ozone resistance is increased. However, according to the above-described synthesis method, a phthalocyanine dye where the number of electron-

withdrawing groups introduced is small, namely, the oxidation potential is baser, is inevitably mingled. Therefore, in order to improve the ozone resistance, it is preferred to use a synthesis method where the production of a compound having a baser oxidation potential is suppressed.

The phthalocyanine compound represented by formula (II) for use in the present invention can be synthesized, for example, by reacting a phthalonitrile derivative (Compound P) shown below and/or a diiminoisoindoline derivative (Compound Q) shown below with a metal derivative represented by formula (III) or can be derived from a tetrasulfophthalocyanine compound obtained by reacting a 4-sulfophthalonitrile derivative (Compound R) shown below with a metal derivative represented by formula (III).



In the formulae above, X_p corresponds to X_{11}, X_{12}, X_{13} or X_{14} in formula (II) and Y_q and $Y_{q'}$ each corresponds to Y_{11}, Y_{12}, Y_{13}, Y_{14}, Y_{15}, Y_{16}, Y_{17} or Y_{18} in formula (II). In

Compound R, M' represents cation.

Examples of the cation represented by M' include alkali metal ions such as Li, Na and K, and organic cations such as triethylammonium ion and pyridinium ion.

Formula (III):

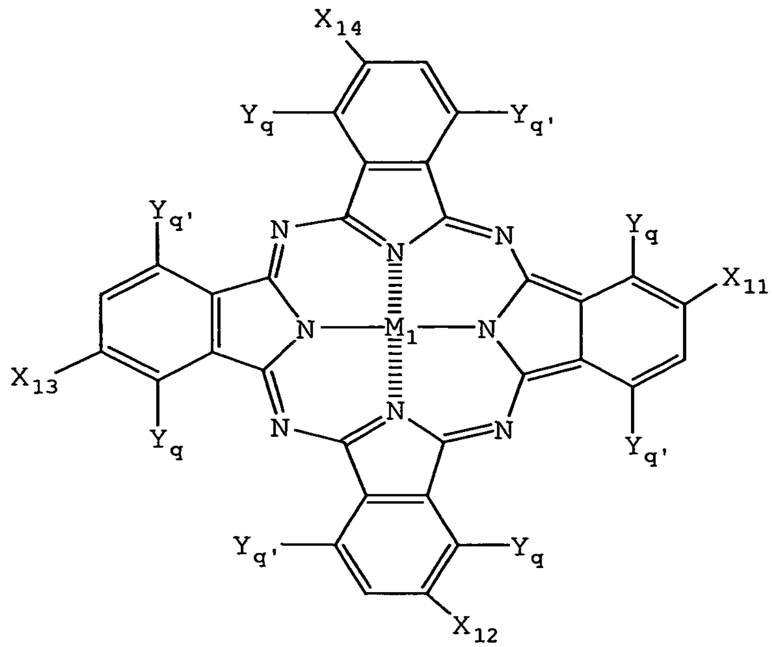
$$M-(Y)_d$$

wherein M has the same meaning as M in formulae (I) and (II), Y represents a monovalent or divalent ligand such as halogen atom, acetate anion, acetylacetonate and oxygen, and d represents an integer of 1 to 4.

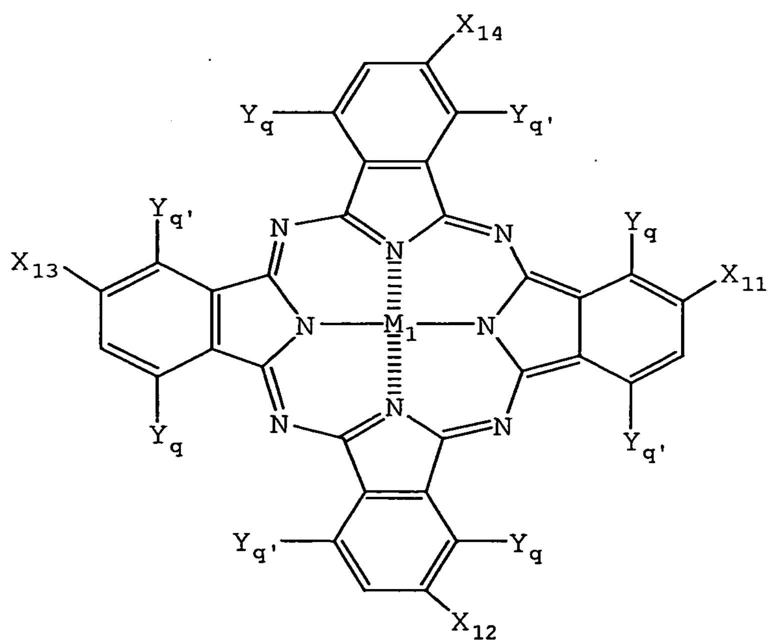
That is, according to this synthesis method, a specific number of desired substituents can be introduced. Particularly, in the case of introducing a large number of electron-withdrawing groups so as to render the oxidation potential more positive as in the present invention, this synthesis method is very excellent as compared with the above-described method for synthesizing the phthalocyanine compound of formula (I).

The thus-obtained phthalocyanine compound represented by formulae (II) is usually a mixture of compounds represented by the following formulae (a)-1 to (a)-4 which are isomers with respect to the substitution site of each X_p, namely, a β-position substitution type.

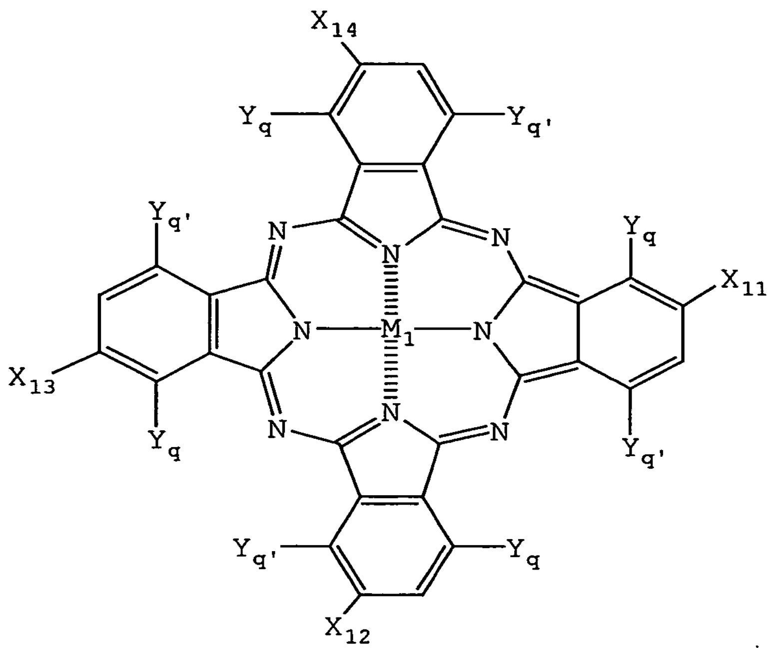
Formula (a)-1:



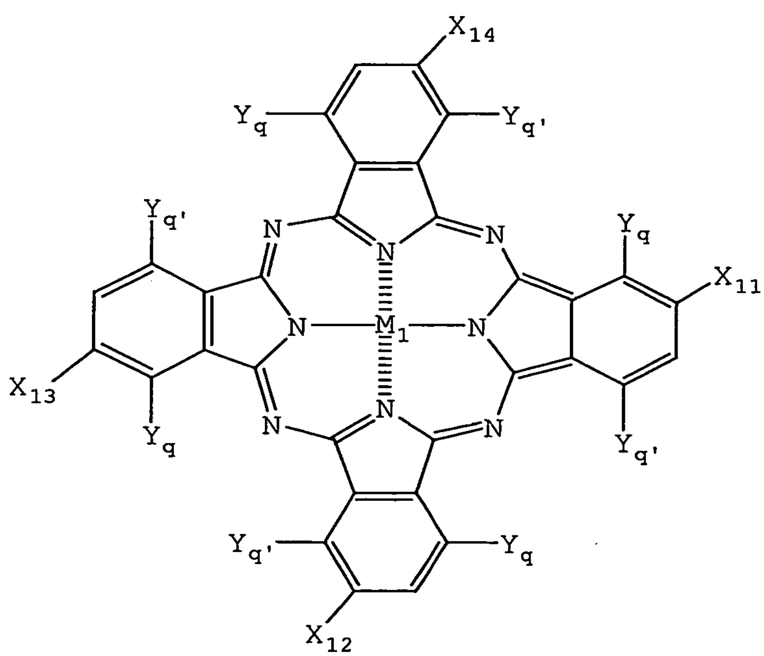
Formula (a)-2:



Formula (a)-3:



Formula (a)-4:



In the synthesis method above, when all X_ps are the same, a β-position substitution type phthalocyanine dye

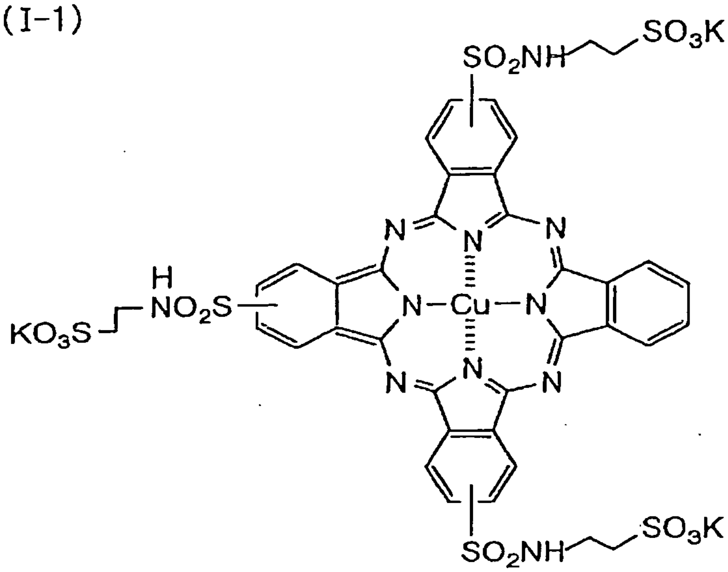
where X_{11}, X_{12}, X_{13} and X_{14} are completely the same substituents can be obtained. On the other hand, when X_ps are different, a dye having substituents of the same kind but partially different from each other or a dye having substituents different from each other can be synthesized. Among the dyes of formula (II), these dyes having electron-withdrawing substituents different from each other are preferred because the solubility and aggregating property of dye and the aging stability of ink can be controlled.

In the present invention, it has been found very important for the improvement of fastness that in any substitution type, the oxidation potential is more positive than 1.0 V (vs SCE), particularly more positive than 1.2 V (vs SCE). The great effect thereof cannot be expected at all from the above-described known techniques. Furthermore, although the detailed mechanism is not known, there is a tendency that the β-position substitution type is apparently more excellent in the color hue, light fastness, ozone gas resistance and the like than the α,β-position mixed substitution type.

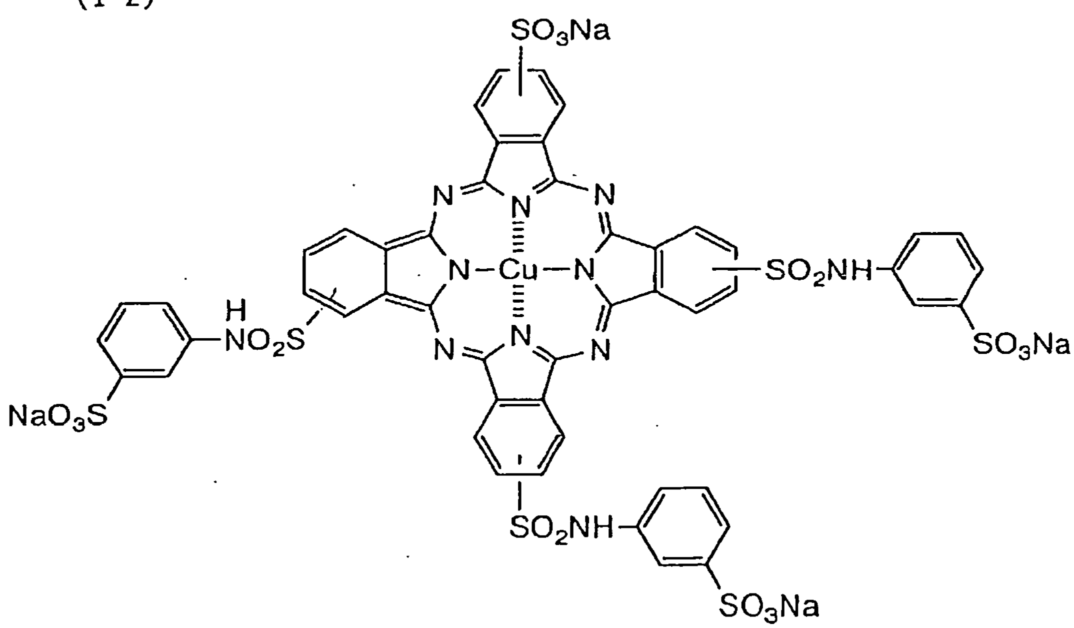
Specific examples (Compounds I-1 to I-12 and 101 to 190) of the phthalocyanine dyes represented by formulae (I) and (II) are set forth below, but the phthalocyanine dye which is preferably used in the present invention is not limited to the following examples.

Compounds:

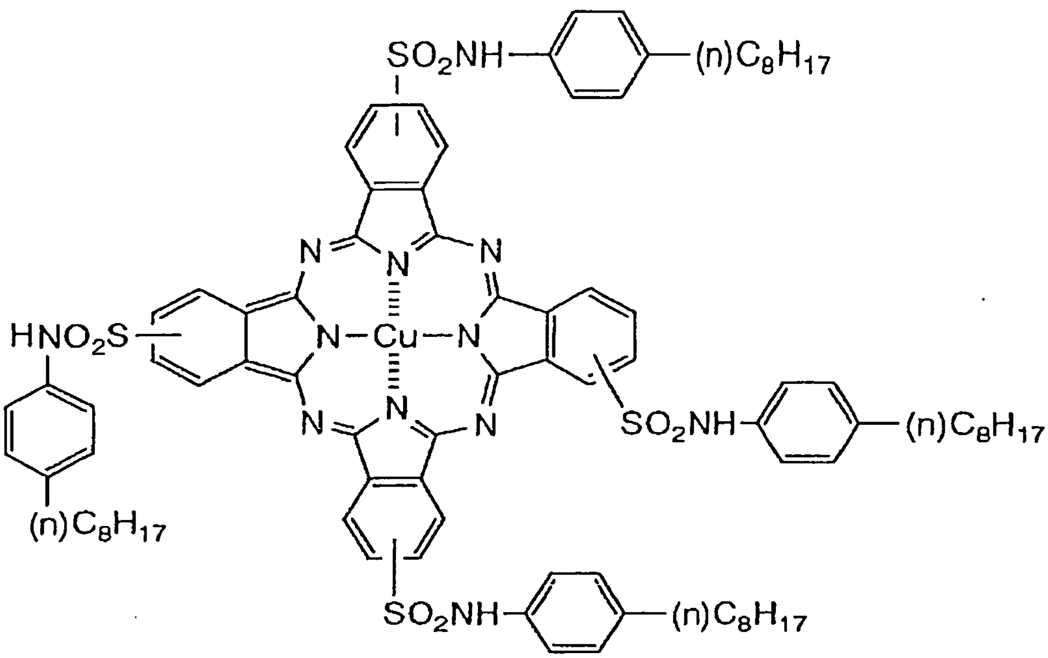
(I-1)



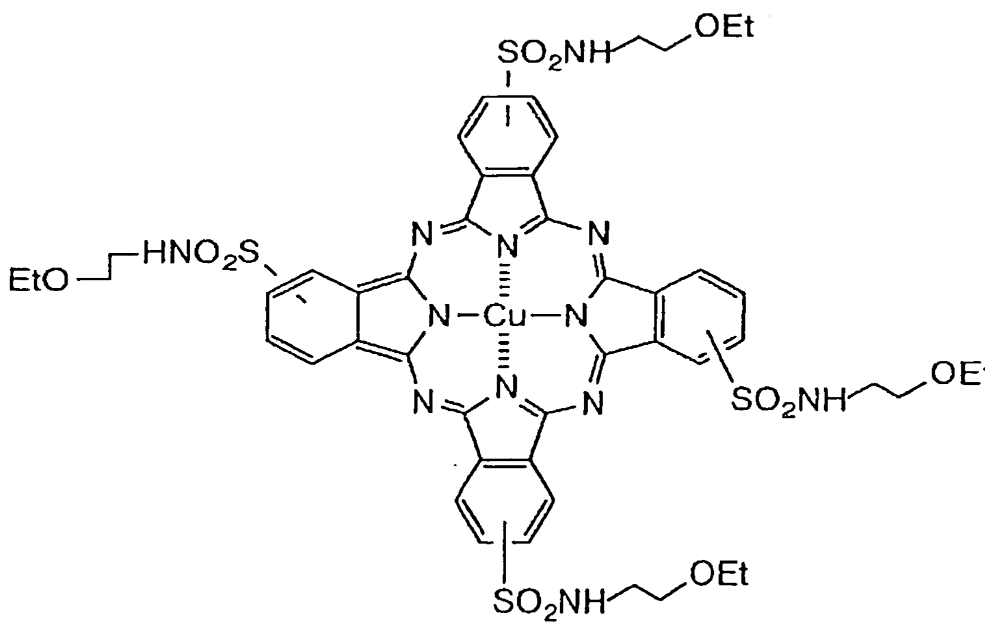
(I-2)



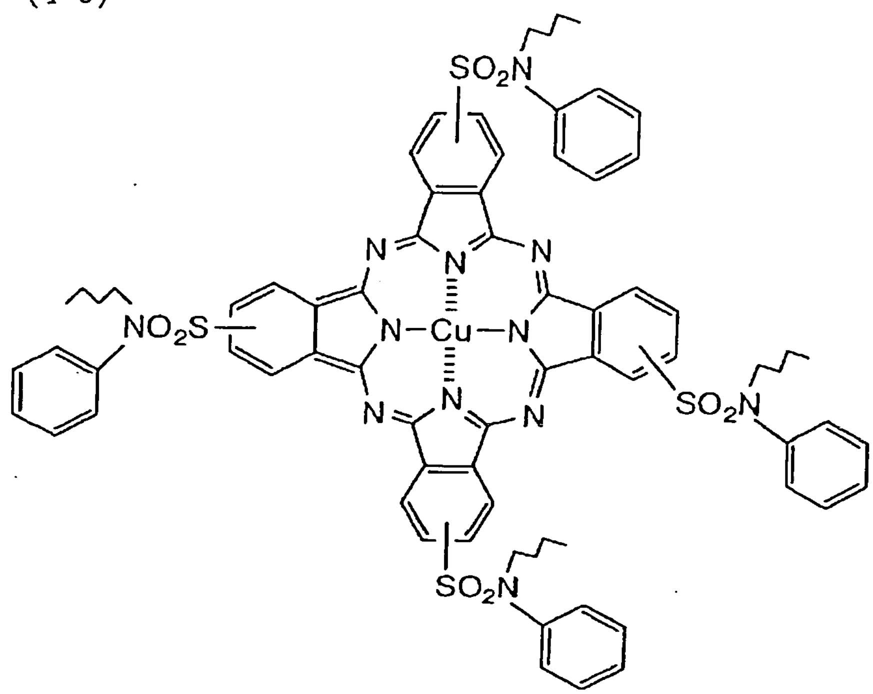
(I-3)



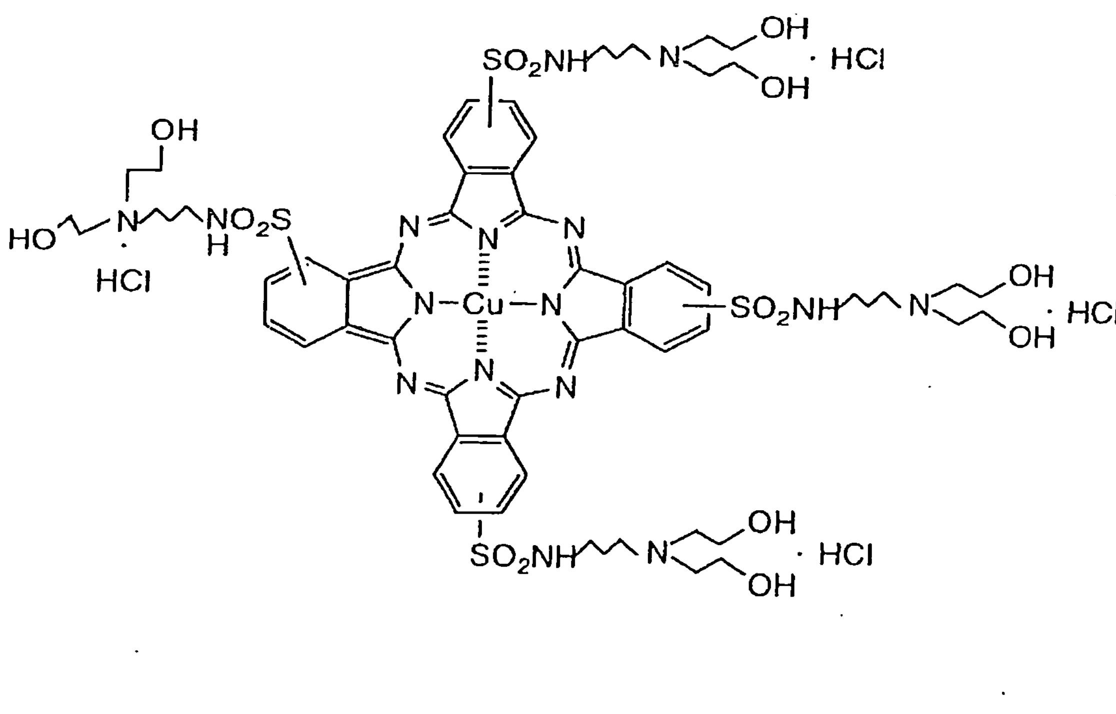
(I-4)



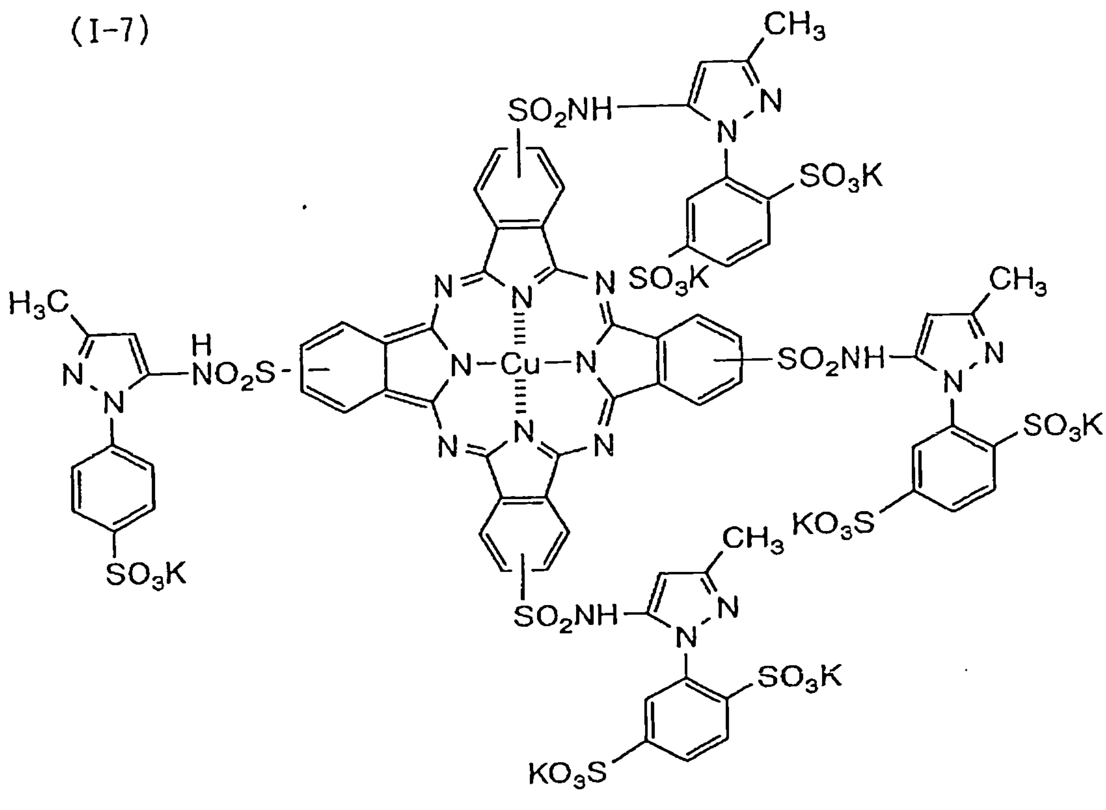
(I-5)



(I-6)

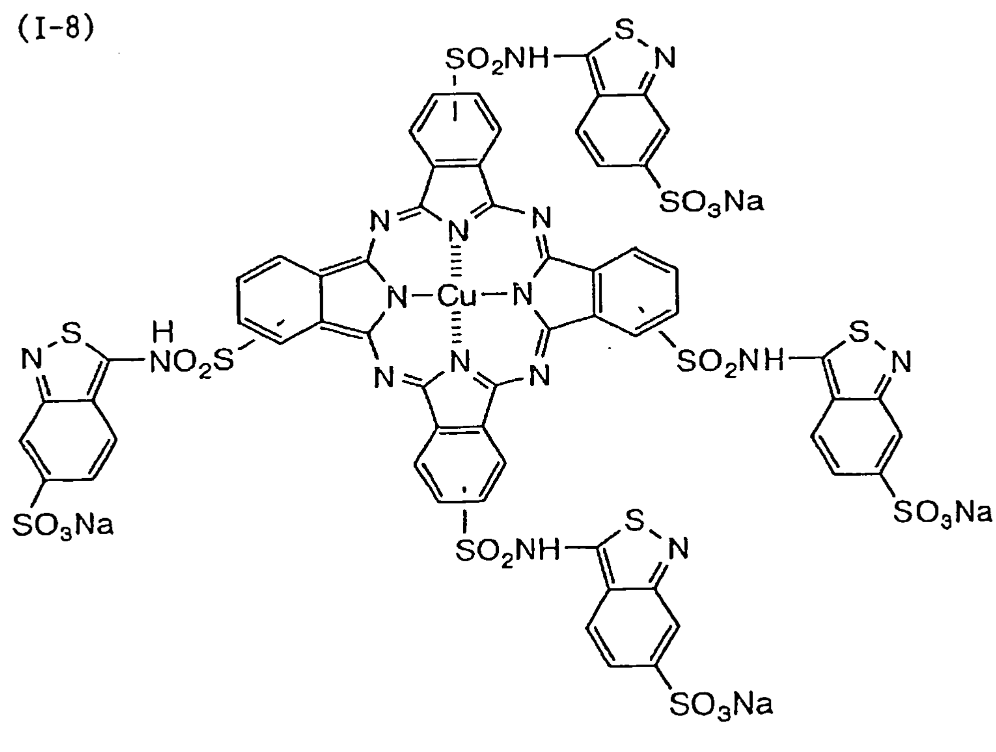


(I-7)



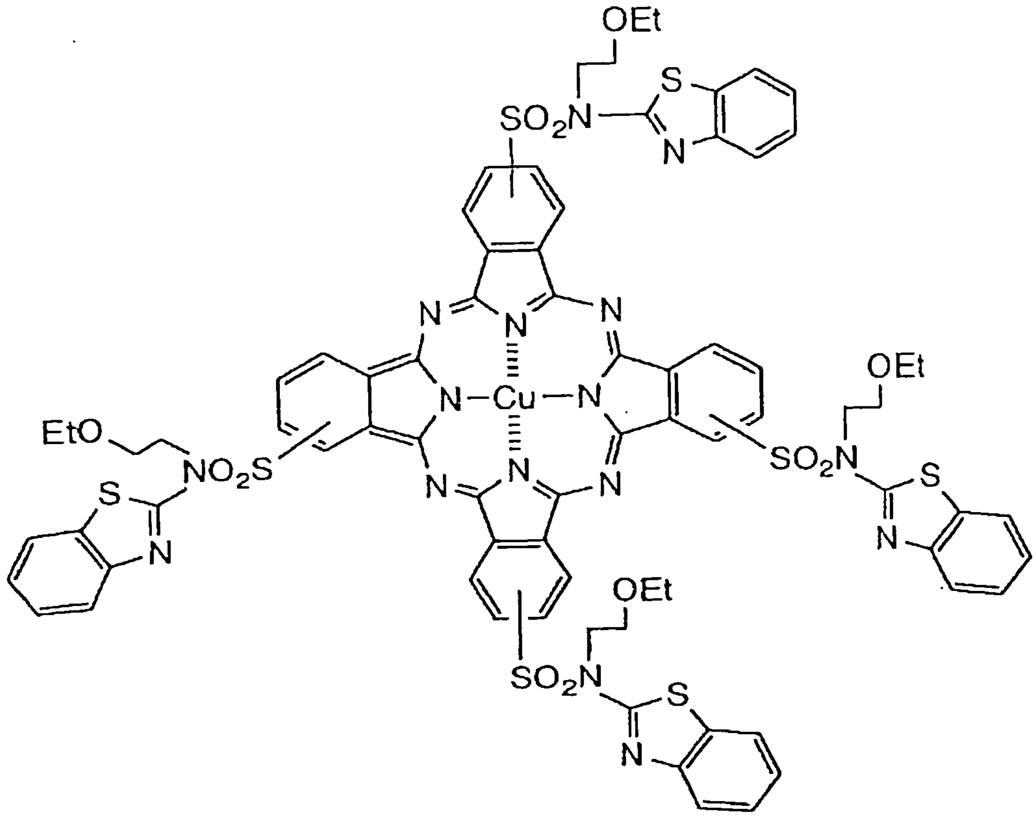
CH3
SO2NH
N
N
SO3K
SO3K
N
N
N
CH3
H3C
H
NO2S
N
N
N
Cu
N
SO2NH
N
N
N
N
N
SO3K
KO3S
SO3K
CH3
SO2NH
N
N
SO3K
KO3S

(I-8)

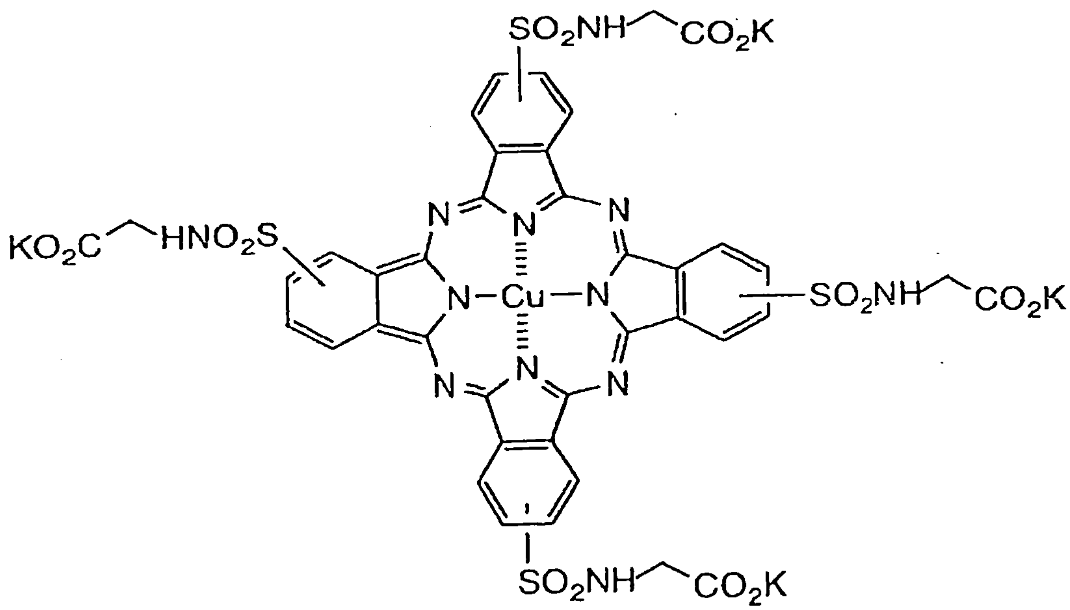


SO2NH
S
N
SO3Na
N
N
N
Cu
N
N
S
H
NO2S
SO2NH
S
N
N
N
N
SO3Na
SO3Na
SO2NH
S
N
SO3Na

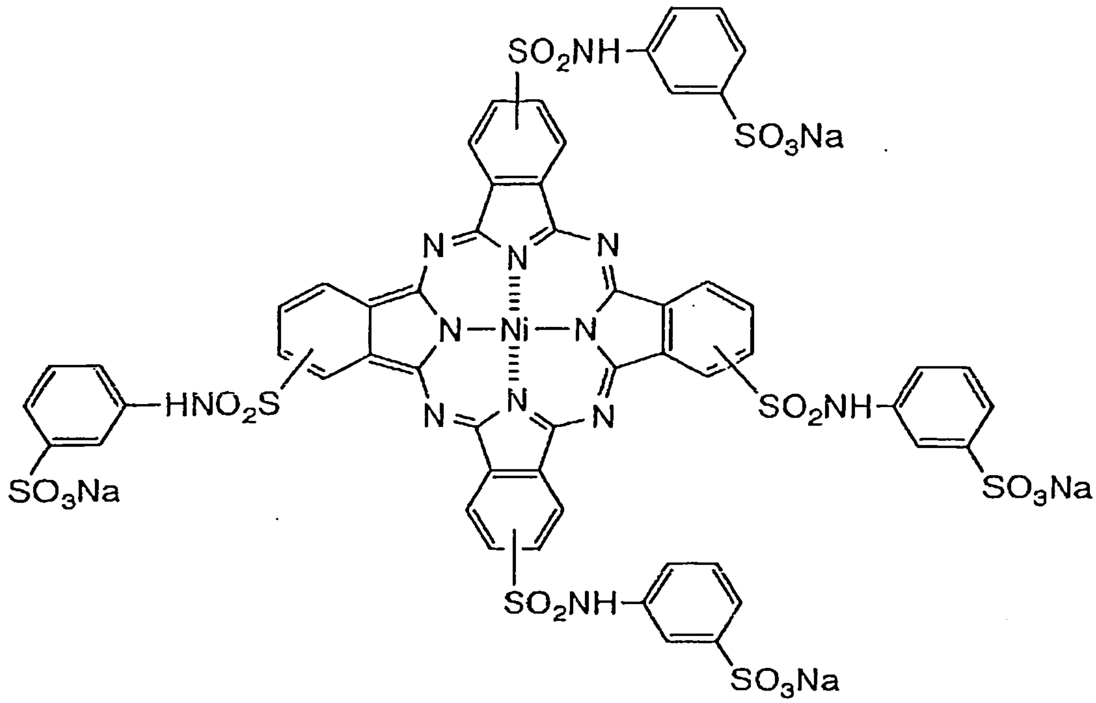
(I-9)



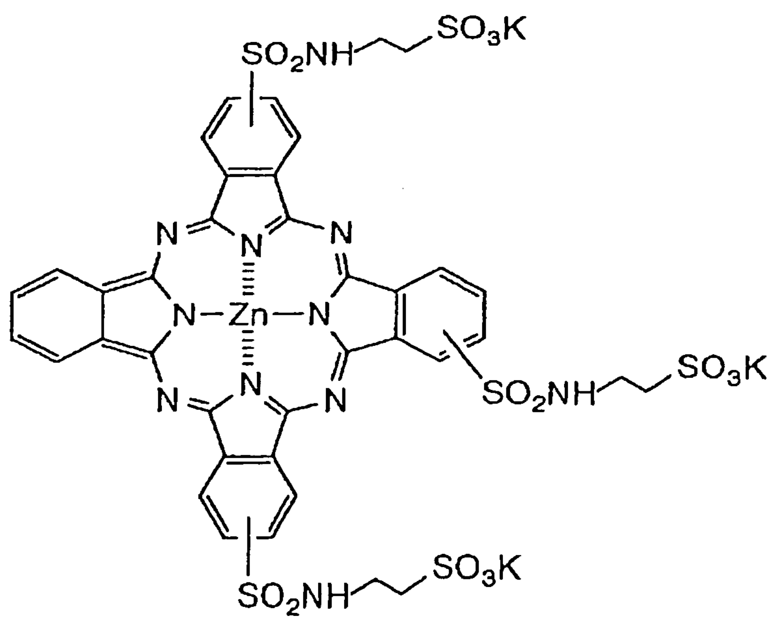
(I-10)

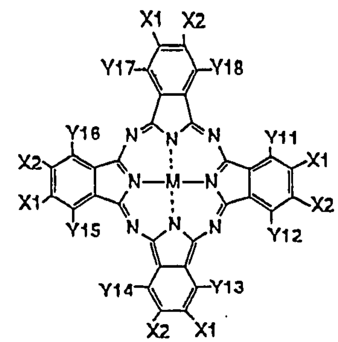


(I-11)


SO2NH
SO3Na
N
N
N
Ni
N
N
HNO2S
N
N
SO2NH
SO3Na
SO3Na
SO2NH
SO3Na

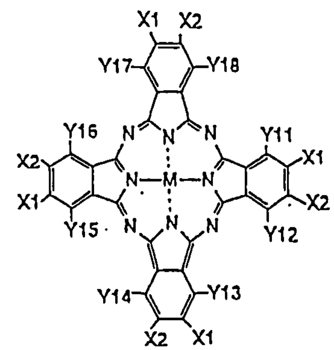
(I-12)


SO2NH
SO3K
N
N
N
Zn
N
N
N
N
SO2NH
SO3K
SO2NH
SO3K



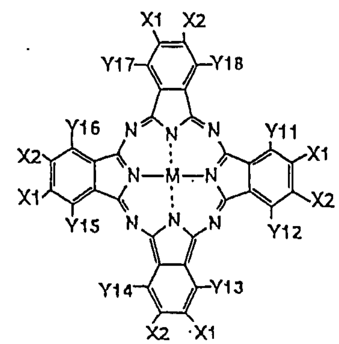
In the following Tables, specific examples of each pair of (X_1, X_2), (Y_{11}, Y_{12}), (Y_{13}, Y_{14}), (Y_{15}, Y_{16}) and (Y_{17}, Y_{18}) are independently in an irregular order.

Compound.No	M	X1	X2	Y11、Y12	Y13、Y14	Y15、Y16	Y17、Y18
101	Cu	$-SO_2-NH-CH_2-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
102	Cu	$-SO_2-NH-CH_2-CH(OH)-CO-NH-CH_2CH_2-SO_3Na$	-H	-Cl, -H	-Cl, -H	-Cl, -H	-Cl, -H
103	Cu	$-SO_2-NH-CH_2-CH_2-CH_2-SO_2NH-CH_2CH(OH)-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
104	Cu	$-SO_2-NH-C_6H_4-SO_2NH-CH_2CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
105	Ni	$-SO_2-NH-CH_2-CH_2-CO-NH-CH(CH_2-COONa)-COONa$	-H	-Cl, -H	-Cl, -H	-Cl, -H	-Cl, -H
106	Cu	$-SO_2-NH-CH_2-CH_2-SO_2-NH-CH_2-COONa$	-CN	-H, -H	-H, -H	-H, -H	-H, -H
107	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH(CH_2-OH)-COOLi$	-H	-H, -H	-H, -H	-H, -H	-H, -H
108	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
109	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_3K$	-H	-H, -H	-H, -H	-H, -H	-H, -H
110	Cu	$-SO_2-(CH_2)_5-CO_2K$	-H	-H, -H	-H, -H	-H, -H	-H, -H



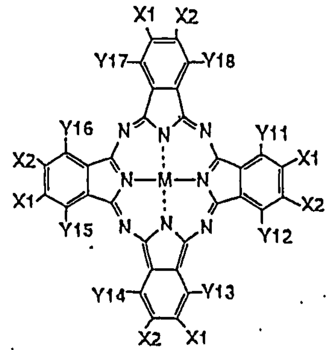
In the following Tables, specific examples of each pair of (X_1, X_2), (Y_{11}, Y_{12}), (Y_{13}, Y_{14}), (Y_{15}, Y_{16}) and (Y_{17}, Y_{18}) are independently in an irregular order.

Compound.No	M	X1	X2	Y11、Y12	Y13、Y14	Y15、Y16	Y17、Y18
111	Cu	$-SO_2-NH-CH_2-CH_2-CH_2-SO_2-NH-CH_2CH(OH)-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
112	Cu	$-SO_2-NH-CH_2-CH_2-CH_2-SO_2NH-CH_2-CH(OH)-CH_3$	$-SO_3Li$	-H, -H	-H, -H	-H, -H	-H, -H
113	Cu	$-SO_2-CH_2-CH(OH)-CH_2SO_3K$	-H	-H, -H	-H, -H	-H, -H	-H, -H
114	Cu	$-SO_2-CH_2-CH(OH)-CH_3$	$-SO_3Li$	-H, -H	-H, -H	-H, -H	-H, -H
115	Cu	$-SO_2NH(CH_2)_3\overset{\oplus}{N}(CH_3)(CH_2CH_2OH)_2 \cdot CH_3-C_6H_4-SO_3^{\ominus}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
116	Cu	$-CO-NH-CH_2-CH(OH)-CH_2SO_3K$	-H	-H, -H	-H, -H	-H, -H	-H, -H
117	Cu	$-CO-NH-CH(COOLi)-CH_2CH_2SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H

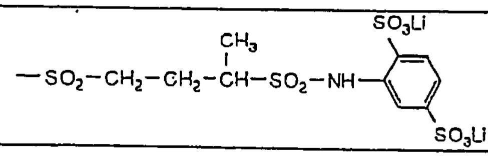


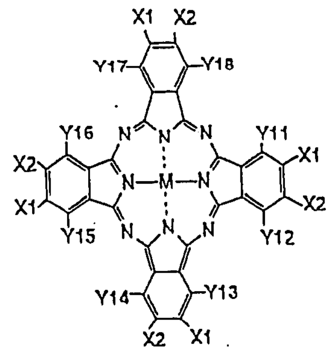
In the following Tables, specific examples of each pair of (X_1, X_2), (Y_{11}, Y_{12}), (Y_{13}, Y_{14}), (Y_{15}, Y_{16}) and (Y_{17}, Y_{18}) are independently in an irregular order.

Compound.No	M	X1	X2	Y11、Y12	Y13、Y14	Y15、Y16	Y17、Y18
118	Cu	$-SO_2CH_2CH_2CH(CH_3)(SO_3Li)$	-H	-H, -H	-H, -H	-H, -H	-H, -H
119	Cu	$-SO_2-CH_2-CH(OH)-CH_2-SO_3Na$	-H	-H, -H	-H, -H	-H, -H	-H, -H
120	Cu	$-SO_2-CH_2-CH_2-CH(CH_3)-COOLi$	-H	-H, -H	-H, -H	-H, -H	-H, -H
121	Cu	$-SO_2(CH_2)_3SO_2NHCH_2-CH(OH)-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
122	Cu	$-CO_2CH_2CH_2CH_2SO_2-NH-CH_2-CH(OH)-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
123	Cu	$-SO_2NH-C_8H_{17}(t)$	-H	-H, -H	-H, -H	-H, -H	-H, -H
124	Cu	$-SO_2-NH-CH_2-CH(CH_2CH_3)-CH_2CHCH_2-CH_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H

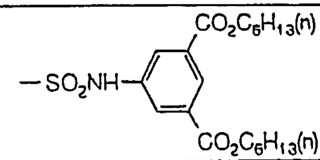
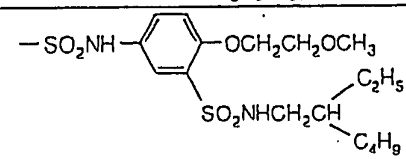
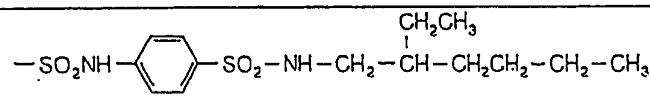
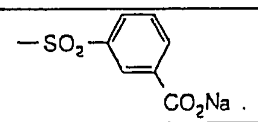
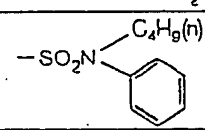


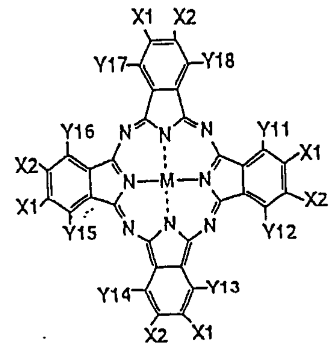
In the following Tables, specific **examples** of each pair of (X_1, X_2), (Y_{11}, Y_{12}), (Y_{13}, Y_{14}), (Y_{15}, Y_{16}) and (Y_{17}, Y_{18}) are independently in an irregular order.

Compound.No	M	X1	X2	Y11、Y12	Y13、Y14	Y15、Y16	Y17、Y18
125	Cu	$-SO_2CH_2CH_2CH_2SO_2-NH-CH_2-CH(CH_3)-CH_2-CH_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H
126	Cu	$-SO_2-CH_2-CH_2-CH_2-CO_2-CH(CH_3)-CH_2-O-CH_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H
127	Cu	$-SO_2CH_2CH_2CH_2SO_2NHCH_2CH_2CH_2O-CH(CH_3)_2$	-H	-H, -H	-H, -H	-H, -H	-H, -H
128	Zn	$-SO_2-CH_2-CH(O-CH_3)-CH_2-O-CH_3$	-CN	-H, -H	-H, -H	-H, -H	-H, -H
129	Cu	$-CO-NH-CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2CH_3$	-H	-Cl, -H	-Cl, -H	-Cl, -H	-Cl, -H
130	Cu	$-CO_2-CH(CH_3)-CH_2-O-C_4H_9(t)$	-H	-H, -H	-H, -H	-H, -H	-H, -H
131	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H

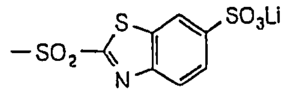
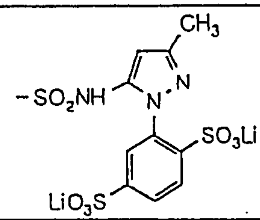
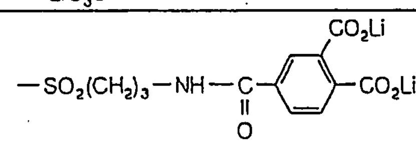
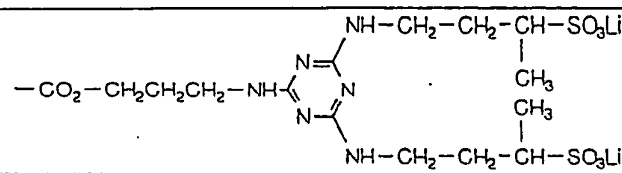


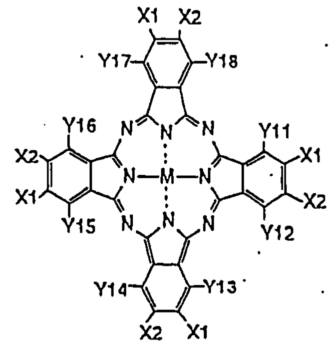
In the following Tables, specific **examples** of each pair of (X_1, X_2), (Y_{11}, Y_{12}), (Y_{13}, Y_{14}), (Y_{15}, Y_{16}) and (Y_{17}, Y_{18}) are independently in an irregular order.

Compound.No	M	X1	X2	Y11、Y12	Y13、Y14	Y15、Y16	Y17、Y18
132	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
133	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
134	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
135	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
136	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H

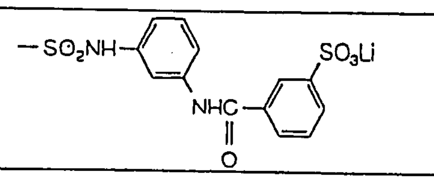
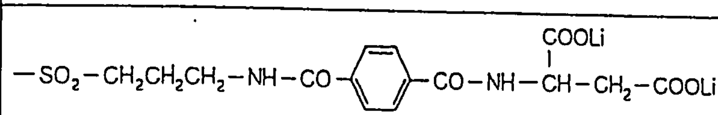


In the following Tables, specific examples of each pair of (X_1, X_2), (Y_{11}, Y_{12}), (Y_{13}, Y_{14}), (Y_{15}, Y_{16}) and (Y_{17}, Y_{18}) are independently in an irregular order.

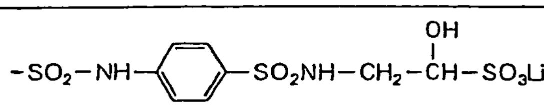
Compound.No	M	X1	X2	Y11、Y12	Y13、Y14	Y15、Y16	Y17、Y18
137	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
138	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
139	Cu		-Cl	-H, -H	-H, -H	-H, -H	-H, -H
140	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H



In the following Tables, specific **examples** of each pair of (X_1, X_2), (Y_{11}, Y_{12}), (Y_{13}, Y_{14}), (Y_{15}, Y_{16}) and (Y_{17}, Y_{18}) are independently in an irregular order

Compound.No	M	X1	X2	Y11、Y12	Y13、Y14	Y15、Y16	Y17、Y18
141	Cu	$-SO_2NH-CH(COONa)-CH_2-CO-N-(CH_2CH_2OH)_2$	-H	-H, -H	-H, -H	-H, -H	-H, -H
142	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
143	Cu	$-CO-NH-CH_2-CH(OH)-CO-NH-CH(COOK)-CH_2CH_2-SO_3K$	-H	-H, -H	-H, -H	-H, -H	-H, -H
144	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
145	Cu	$-SO_2CH_2CH_2OCH_2CH_2OCH_2CH_2SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H

M-Pc$(X_{p1})_m(X_{p2})_n$ In the following Tables, introduction sites of respective substituents (Xp_1) and (Xp_2) are in an irregular order within the β-position substitution type.

Compound No.	M	Xp1 (upper stand) / Xp2 (lower stand)	m	n
146	Cu	$-SO_2-NH-CH_2-CH(CH_3)-SO_3Li$	3	1
		$-SO_2-NH-CH_2-CH(OH)-CH_3$		
147	Cu	$-SO_2-NH-CH_2-CH_2SO_3Li$	3	1
		$-SO_2-NH-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$		
148	Cu	$-SO_2-NH-CH_2-CH(CH_3)-SO_3Li$	3	1
		$-SO_2NH-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH_2-O-CH_2-CH_2-OH$		
149	Cu	$-SO_2-NH-CH_2-CH(CH_3)-SO_3Li$	2	2
		$-SO_2-NH-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-OH)_2$		
150	Cu	$-SO_2-NH-CH_2-CH_2-SO_2-NH-CH_2CH_2-COONa$	3	1
		$-SO_2NH-CH(CH_3)-CH_2OH$		
151	Cu		3	1
		$-SO_2NH-CH_2-CH_2-O-CH_2-CH_2-OH$		

$M\text{-}Pc(X_{p1})_m(X_{p2})_n$ In the following Tables, introduction sites of respective substituents (Xp_1) and (Xp_2) are in an irregular order within the β-position substitution type.

Compound No.	M	Xp1(upper stand)/Xp2(lower stand)	m	n
152	Cu	$-SO_2-CH_2-CH_2-CH(CH_3)-SO_3Li$	2.5	1.5
		$-SO_2-CH_2-CH_2-O-CH_2-CH_2-OH$		
153	Cu	$-SO_2-CH_2-CH_2-CH(CH_3)-SO_3Na$	2	2
		$-SO_2-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-OH)_2$		
154	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_3Li$	3	1
		$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$		
155	Cu	$-SO_2-CH_2-CH_2-CH_2-COOK$	2	2
		$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_2-COOK$		
156	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_3Li$	3	1
		$-SO_2-CH_2-CH(OH)-CH_2-SO_3Li$		
157	Cu	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-SO_3Li$	2	2
		$-SO_2-CH_2-CH_2-CH_2-CO_2-CH_2-CH_2-CH(OH)-CH_2-COOK$		

M-Pc$(X_{p1})_m(X_{p2})_n$ In the following Tables, introduction sites of respective substituents (Xp_1) and (Xp_2) are in an irregular order within the β-position substitution type.

Compound No.	M	Xp1 (upper stand)/Xp2 (lower stand)	m	n
158	Cu	$-SO_2-CH_2-CH(OH)-CH_2SO_3Li$ $-SO_2-CH_2-C_6H_4-SO_2NH-CH_2-CH(OH)-CH_2-OH$	3	1
159	Cu	$-SO_2NHCH_2CH_2-SO_3Li$ $-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	3	1
160	Cu	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-SO_3Na$ $-SO_2-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-COONa)-CH_2-COONa$	3	1
161	Cu	$-SO_2CH_2CH_2CH_2SO_3Li$ $-SO_2CH_2CH_2CH_2SO_2NHCH_2-CH(OH)-CH_2SO_3Li$	3	1
162	Cu	$-SO_2CH_2CH_2CH_2SO_3Li$ $-SO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OH$	2	2
163	Cu	$-SO_2CH_2CH_2CH_2SO_3K$ $-SO_2CH_2CH_2CH_2SO_2NH-CH(CH_3)-CH_2-OH$	3	1

$M\text{-}Pc(X_{p1})_m(X_{p2})_n$ In the following Tables, introduction sites of respective substituents (Xp_1) and (Xp_2) are in an irregular order within the β-position substitution type.

Compound No.	M	Xp1(upper stand)/Xp2(lower stand)	m	n
164	Cu	$-SO_2CH_2CH_2CH_2SO_3Li$ $-SO_2CH_2CH_2CH_2SO_2N(CH_2CH_2OH)_2$	2	2
165	Cu	$-CO-NH-CH_2-CH_2-SO_3K$ $-CO-NH-CH_2-CH_2-O-CH_2-CH_2-OH$	3	1
166	Cu	$-CO-NH-CH_2-CH_2-SO_2-NH-CH_2-CH_2-COONa$ $-CO-NH-CH_2-CH(OH)-CH_3$	3	1
167	Cu	$-SO_2(CH_2)_3SO_2NHCH_2-CH(OH)-CH_2CO_2Li$ $-CO-NH-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-OH)_2$	2.5	1.5
168	Cu	$-CO_2-CH_2-CH_2-CH(CH_3)-SO_3Na$ $-CO-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-OH)_2$	2	2
169	Cu	$-CO_2-CH_2-CH_2-CH_2-SO_3Li$ $-CO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	3	1
170	Cu	$-CO_2-CH_2-CH_2-CH_2COOK$ $-CO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_2-COOK$	2	2

M-Pc$(X_{p1})_m(X_{p2})_n$ In the following Tables, introduction sites of respective substituents (Xp_1) and (Xp_2) are in an irregular order within the β-position substitution type.

Compound No.	M	Xp1 (upper stand) / Xp2 (lower stand)	m	n
171	Cu	$-CO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-SO_3Na$	3	1
		$-SO_2-CH_2-C_6H_4-SO_2NH-CH_2-CH(OH)-CH_2-OH$		
172	Cu	$-SO_2CH_2CH_2OCH_2CH_2O-CH_2CH_2SO_3K$	2	2
		$-CO_2-CH_2-CH_2-CH_2-CO_2-CH_2-CH_2-CH(OH)-CH_2-COOK$		
173	Cu	$-SO_2(CH_2)_3SO_2NHCH_2CH(OH)CH_2OH$	2	2
		$-CO_2-CH_2-CH(OH)-CH_2-SO_3Li$		
174	Cu	$-SO_2(CH_2)_3SO_2NHCH_2-CH(OH)-CH_2SO_3K$	3	1
		$-CO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$		
175	Cu	$-SO_2(CH_2)_3SO_2NH(CH_2)_3N(CH_2CH_2OH)_2$	2	2
		$-CO_2-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-COOLi)-CH_2-COOLi$		
176	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	3	1
		$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(CH_2CH_3)-CH_2CH_2-CH_2CH_3$		

M-Pc$(X_{p1})_m(X_{p2})_n$ In the following Tables, introduction sites of respective substituents (Xp_1) and (Xp_2) are in an irregular order within the β-position substitution type.

Compound No.	M	Xp1 (upper stand) / Xp2 (lower stand)	m	n
177	Cu	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$	2	1
		$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-\overset{OH}{\overset{\vert}{C}}H-CH_3$		
178	Cu	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH$	3	1
		$-SO_2-CH_2-CH_2-CH_2-CO_2-CH_2-\overset{CH_2CH_3}{\overset{\vert}{C}}H-CH_2CH_2-CH_2CH_3$		
179	Cu	$-SO_2-CH_2-\overset{CH_2CH_3}{\overset{\vert}{C}}H-CH_2CH_2-CH_2CH_3$	2	2
		$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-\overset{O-CH_3}{\overset{\vert}{C}}H-CH_3$		
180	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-\overset{O-CH_3}{\overset{\vert}{C}}H-CH_3$	3	1
		$-SO_2NH-CH_2-CH_2-SO_2NH-CH_2-CH_2-O-CH_2-CH_2-OH$		
181	Cu	$-SO_2-CH_2-CH_2-CH_2-CO_2-NH-\overset{CH_3}{\overset{\vert}{C}}H-CH_2-CH_3$	3	1
		$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH(CH_3)_2$		
182	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2NH-CH_2-\overset{OH}{\overset{\vert}{C}}H-CH_3$	2.5	1.5
		$-SO_2-CH_2-CH_2-CH_2-CO_2-NH-\overset{CH_3}{\overset{\vert}{C}}H-CH_2-CH_3$		

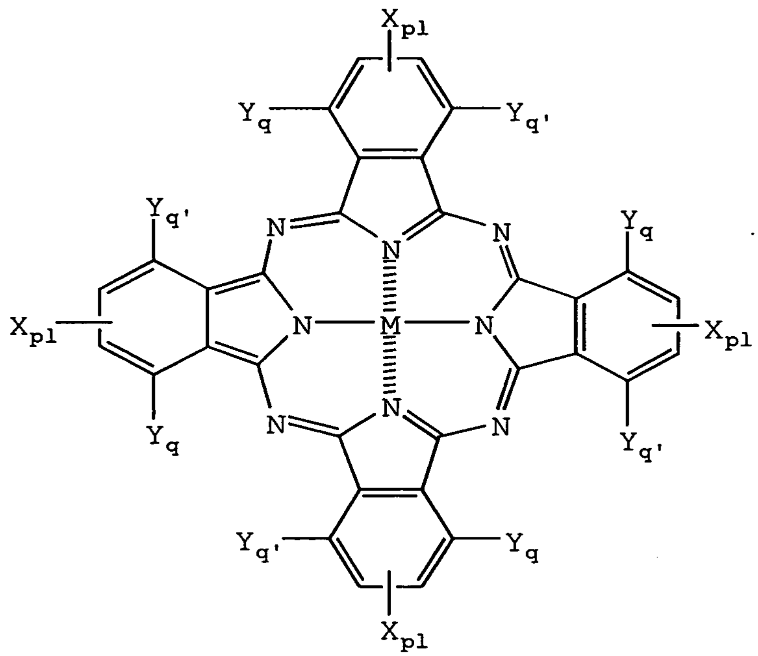
$M\text{-}Pc(X_{p1})_m(X_{p2})_n$ In the following Tables, introduction sites of respective substituents (Xp_1) and (Xp_2) are in an irregular order within the β-position substitution type.

Compound No.	M	Xp1 (upper stand) / Xp2 (lower stand)	m	n
183	Cu	$-SO_2-CH_2-CH_2-CH_2-CO_2-NH-CH(CH_3)-CH_2-CH_3$	2	2
		$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-(CH_2)_3-CH_2-O-CH_2CH_2-OH$		
184	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	3	1
		$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$		
185	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	3	1
		$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$		
186	Cu	$-SO_2-CH_2-CH_2-CH_2-CO_2-NH-CH(CH_3)-CH_2-CH_3$	3	1
		$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH$		
187	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH(CH_3)_2$	3	1
		$-CO_2-CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2CH_3$		
188	Cu	$-CO_2-CH_2-CH_2-CH_2-CO_2-NH-CH(CH_3)-CH_2-CH_3$	3	1
		$-CO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$		

$M-Pc(X_{p1})_m(X_{p2})_n$ In the following Tables, introduction sites of respective substituents (Xp_1) and (Xp_2) are in an irregular order within the β-position substitution type.

Compound No.	M	Xp1(upper stand)/Xp2(lower stand)	m	n
189	Cu	$-CO-NH-CH_2-CH_2-CH_2-SO_2-NH-CH(CH_3)_2$	3	1
		$-SO_2-NH-CH_2-\overset{CH_2CH_3}{\overset{\vert}{CH}}-CH_2-CH_2-CH_2-CH_3$		
190	Cu	$-CO-NH-CH_2-\overset{CH_2CH_3}{\overset{\vert}{CH}}-CH_2-CH_2-CH_2CH_3$	3	1
		$-CO-NH-CH_2-CH_2-O-CH_2-CH_2-CH_3$		

The structure of the phthalocyanine compound represented by M-Pc$(X_{p1})_m(X_{p2})_n$ in Compound Nos. 146 to 190 is shown below:



(wherein each X_{p1} is independently X_{p1} or X_{p2}).

The phthalocyanine dye represented by formula (I) can be synthesized according to the patent publications described above. Furthermore, the phthalocyanine dye represented by formula (II) can be synthesized by the methods described in JP-A-2001-226275, JP-A-2001-96610, JP-A-2001-47013 and JP-A-2001-193638, in addition to the above-described synthesis method. The starting material, dye intermediate and synthesis route are not limited to those described in these patent publications.

In the cyan ink set for inkjet recording for use in the present invention, at least one constituent ink

preferably contains at least one phthalocyanine dye described above by dissolving or dispersing it in an aqueous medium. In this case, the phthalocyanine dye is contained in an amount of 0.2 to 20 weight %, more preferably from 0.5 to 15 weight %.

As described above regarding the magenta ink set, in preparing an ink set comprising two or more inks sharing the main absorption region, generally, one ink is produced as a light-type thin ink and another is produced as a thick ink. In this case, the absorbance of light ink and the absorbance of dark ink are in the above-described relationship.

In each constituent ink, the dye represented by formula (1) may be used alone but in the case of using the dye in combination with other colorants, the colorant combined may be either a dye or a pigment and may be in the form of being dissolved in an aqueous medium or in the form that a pigment insoluble in the aqueous medium is present in the dispersed state. In the case of a pigment, the solubility in water (at 25°C) is 0.1 g/100 g or less in many cases. As for the ink composition where the component is dispersed, examples of the component include an emulsion dispersion, a polymer dye, a dye supported on or dispersed in a polymer, and a pigment. Among these, a pigment is preferred.

Also, the dye ink may contain a water-insoluble pigment in the dispersed state or the pigment ink may contain a water-soluble dye.

When a dye represented by formula (1) and a different dye or a pigment are present in combination in one ink composition, the total concentration thereof is from 0.2 to 20 weight %, preferably from 0.5 to 15 weight %.

In the ink set of the present invention for the magenta ink having a main spectral absorption region of 500 to 580 nm or for the cyan ink having a main spectral adsorption region of 580 to 680 nm, in addition to the specific preferred dye of formula (1) or (I) for use in the present invention, other dyes may be added for the purpose of, for example, adjusting the color tone. As for the dye which can be used together in addition to the dye represented by formula (1) or (I), dyes known in this field such as triarylmethane dye, anthraquinone dye, anthrapyridone dye, azomethine dye, azo dye, cyanine dye, merocyanine dye and oxonol dye can be used individually or in combination.

Also, for constituting an ink set for full color printing, other inks or ink sets such as yellow ink and black ink can be used in combination with the magenta and cyan ink sets of the present invention and in these inks, respective dyes are used.

Examples of the dye which can be used in the ink of an ink set having the same main absorption region or in the ink or ink set combined therewith having a different main absorption region include the followings.

Examples of the yellow dye include aryl- or heteryl-azo dyes having a phenol, a naphthol, an aniline, a pyrazolone, a pyridone or an open chain-type active methylene compound as the coupling component; azomethine dyes having an open chain-type active methylene compound as the coupling component; methine dyes such as benzylidene dye and monomethine oxonol dye; and quinone-base dyes such as naphthoquinone dye and anthraquinone dye. Other examples of the dye species include quinophthalone dye, nitro·nitroso dye, acridine dye and acridinone dye. These dyes may be a dye which provides a yellow color for the first time when a part of the chromophore is dissociated. In this case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in the partial structure.

Examples of the magenta dye include aryl- or heteryl-azo dyes having a phenol, a naphthol or an aniline as the coupling component; azomethine dyes having a pyrazolone or a pyrazolotriazole as the coupling component; methine dyes such as arylidene dye, styryl dye, merocyanine dye and

oxonol dye; carbonium dyes such as diphenylmethane dye, triphenylmethane dye and xanthene dye; quinone-base dyes such as naphthoquinone, anthraquinone and anthrapyridone; and condensed polycyclic dyes such as dioxazine dye. These dyes may be a dye which provides a magenta color for the first time when a part of the chromophore is dissociated. In this case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in the partial structure.

Examples of the cyan dye include azomethine dyes such as indoaniline dye and indophenol dye; polymethine dyes such as cyanine dye, oxonol dye and merocyanine dye; carbonium dyes such as diphenylmethane dye, triphenylmethane dye and xanthene dye; phthalocyanine dyes; anthraquinone dyes; aryl- or heteryl-azo dyes having a phenol, a naphthol or an aniline as the coupling component; and indigo·thioindigo dyes. These dyes may be a dye which provides a cyan color for the first time when a part of the chromophore is dissociated. In this case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in the partial structure.

A black dye such as polyazo dye can also be used.

Examples of the water-soluble dye include a direct dye, an acid dye, a food dye, a basic dye and a reactive dye. Preferred examples thereof include C.I. Direct Red 2, 4, 9, 23, 26, 31, 39, 62, 63, 72, 75, 76, 79, 80, 81, 83, 84, 89, 92, 95, 111, 173, 184, 207, 211, 212, 214, 218, 21, 223, 224, 225, 226, 227, 232, 233, 240, 241, 242, 243 and 247; C.I. Direct Violet 7, 9, 47, 48, 51, 66, 90, 93, 94, 95, 98, 100 and 101; C.I. direct Yellow 8, 9, 11, 12, 27, 28, 29, 33, 35, 39, 41, 44, 50, 53, 58, 59, 68, 86, 87, 93, 95, 96, 98, 100, 106, 108, 109, 110, 130, 132, 142, 144, 161 and 163; C.I. Direct Blue 1, 10, 15, 22, 25, 55, 67, 68, 71, 76, 77, 78, 80, 84, 86, 87, 90, 98, 106, 108, 109, 151, 156, 158, 159, 160, 168, 189, 192, 193, 194, 199, 200, 201, 202, 203, 207, 211, 213, 214, 218, 225, 229, 236, 237, 244, 248, 249, 251, 252, 264, 270, 280, 288, 289 and 291; C.I. Direct Black 9, 17, 19, 22, 32, 51, 56, 62, 69, 77, 80, 91, 94, 97, 108, 112, 113, 114, 117, 118, 121, 122, 125, 132, 146, 154, 166, 168, 173 and 199; C.I. Acid Red 35, 42, 52, 57, 62, 80, 82, 111, 114, 118, 119, 127, 128, 131, 143, 151, 154, 158, 249, 254, 257, 261, 263, 266, 289, 299, 301, 305, 336, 337, 361, 396 and 397; C.I. Acid Violet 5, 34, 43, 47, 48, 90, 103 and 126; C.I. Acid Yellow 17, 19, 23, 25, 39, 40, 42, 44, 49, 50, 61, 64, 76, 79, 110, 127, 135, 143, 151, 159, 169, 174, 190, 195, 196, 197, 199, 218, 219, 222 and 227; C.I. Acid Blue 9, 25, 40, 41, 62, 72, 76, 78, 80, 82,

92, 106, 112, 113, 120, 127:1, 129, 138, 143, 175, 181, 205, 207, 220, 221, 230, 232, 247, 258, 260, 264, 271, 277, 278, 279, 280, 288, 290 and 326; C.I. Acid Black 7, 24, 29, 48, 52:1 and 172; C.I. Reactive Red 3, 13, 17, 19, 21, 22, 23, 24, 29, 35, 37, 40, 41, 43, 45, 49 and 55; C.I. Reactive Violet 1, 3, 4, 5, 6, 7, 8, 9, 16, 17, 22, 23, 24, 26, 27, 33 and 34; C.I. Reactive Yellow 2, 3, 13, 14, 15, 17, 18, 23, 24, 25, 26, 27, 29, 35, 37, 41 and 42; C.I. Reactive Blue 2, 3, 5, 8, 10, 13, 14, 15, 17, 18, 19, 21, 25, 26, 27, 28, 29 and 38; C.I. Reactive Black 4, 5, 8, 14, 21, 23, 26, 31, 32 and 34; C.I. Basic Red 12, 13, 14, 15, 18, 22, 23, 24, 25, 27, 29, 35, 36, 38, 39, 45 and 46; C.I. Basic Violet 1, 2, 3, 7, 10, 15, 16, 20, 21, 25, 27, 28, 35, 37, 39, 40 and 48; C.I. Basic Yellow 1, 2, 4, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 39 and 40; C.I. Basic Blue 1, 3, 5, 7, 9, 22, 26, 41, 45, 46, 47, 54, 57, 60, 62, 65, 66, 69 and 71; and C.I. Basic Black 8.

In the ink composition of the present invention, for adjusting the color tone so as to obtain a full color image, other colorants can be used together with the above-described dye. Examples of the other colorant which can be used together include the following pigments.

As the pigment for use in the present invention, commercially available pigments and known pigments described in various publications can be used. Examples of

the publication include Color Index, compiled by The Society of Dyers and Colourists, Kaitei Shin Han Ganryo Binran (Revised New Handbook of Pigments), compiled by Nippon Ganryo Gijutsu Kyokai (1989), Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Shuppan (1986), Insatsu Ink Gijutsu (Printing Ink Technique), CMC Shuppan (1984), and W. Herbst and K. Hunger, Industrial Organic Pigments, VCH Verlagsgesellschaft (1993). Specific examples of the pigment include organic pigments such as azo pigments (e.g., azo lake pigment, insoluble azo pigment, condensed azo pigment, chelate azo pigment), polycyclic pigments (e.g., phthalocyanine-base pigment, anthraquinone-base pigment, perylene-base or perynone-base pigment, indigo-base pigment, quinacridone-base pigment, dioxazine-base pigment, isoindolinone-base pigment, quinophthalone-base pigment, diketopyrrolopyrrole-base pigment), dyeing lake pigments (lake pigments of acidic or basic dye) and azine pigments, and inorganic pigments such as C.I. Pigment Yellow 34, 37, 42 and 53 which are a yellow pigment, C.I. Pigment Red 101 and 108 which are a red-type pigment, C.I. Pigment Blue 27, 29 and 17:1 which are a blue-type pigment, C.I. Pigment Black 7 and magnetite which are a black-type pigment, and C.I. Pigment White 4, 6, 18 and 21 which are a white-type pigment.

The pigment having a color tone preferred for the

formation of an image includes the followings. As the blue to cyan pigment, phthalocyanine pigments, anthraquinone-type indanthrone pigments (for example, C.I. Pigment Blue 60) and dyeing lake pigment-type triarylcarbonium pigments are preferred, and phthalocyanine pigments are most preferred (preferred examples thereof include copper phthalocyanine such as C.I. Pigment Blue 15:1, 15:2, 15:3, 15:4 and 15:6, monochloro or low chlorinated copper phthalocyanine, aluminum phthalocyanine such as pigments described in European Patent 860475, nonmetallic phthalocyanine such as C.I. Pigment Blue 16, and phthalocyanine with the center metal being Zn, Ni or Ti, and among these, C.I. Pigment Blue 15:3 and 15:4 and aluminum phthalocyanine are more preferred).

As the red to violet pigment, azo pigments (preferred examples thereof include C.I. Pigment Red 3, 5, 11, 22, 38, 48:1, 48:2, 48:3, 48:4, 49:1, 52:1, 53:1, 57:1, 63:2, 144, 146 and 184, and among these, C.I. Pigment Red 57:1, 146 and 184 are more preferred), quinacridone-base pigments (preferred examples thereof include C.I. Pigment Red 122, 192, 202, 207 and 209 and C.I. Pigment Violet 19 and 42, and among these, C.I. Pigment Red 122 is more preferred), dyeing lake pigment-type triarylcarbonium pigments (preferred examples thereof include xanthene-base C.I. Pigment Red 81:1 and C.I. Pigment Violet 1, 2, 3, 27 and

39), dioxazine-base pigments (for example, C.I. Pigment Violet 23 and 37), diketopyrrolopyrrole-base pigments (for example, C.I. Pigment Red 254), perylene pigments (for example, C.I. Pigment Violet 29), anthraquinone-base pigments (for example, C.I. Pigment Violet 5:1, 31 and 33) and thioindigo-base pigments (for example, C.I. Pigment Red 38 and 88) are preferred.

As the yellow pigment, azo pigments (preferred examples thereof include monoazo pigment-type C.I. Pigment Yellow 1, 3, 74 and 98, disazo pigment-type C.I. Pigment Yellow 12, 13, 14, 16, 17 and 83, synthetic azo-type C.I. Pigment 93, 94, 95, 128 and 155, and benzimidazolone-type C.I. Pigment Yellow 120, 151, 154, 156 and 180, and among these, those not using a benzidine-base compound as a raw material are more preferred), isoindoline·isoindolinone-base pigments (preferred examples thereof include C.I. Pigment Yellow 109, 110, 137 and 139), quinophthalone pigments (preferred examples thereof include C.I. Pigment Yellow 138) and flavanthrone pigments (for example, C.I. Pigment Yellow 24) are preferred.

As the black pigment, inorganic pigments (preferred examples thereof include carbon black and magnetite) and aniline black are preferred.

Other than these, an orange pigment (for example, C.I. Pigment Orange 13 and 16) and a green pigment (for example,

C.I. Pigment Green 7) may be used.

The above-described pigment which can be used in the present invention may be used as it is or may be subjected to a surface treatment. For the surface treatment, a method of coating the surface with resin or wax, a method of attaching a surfactant, and a method of binding a reactive substance (for example, a radical generated from a silane coupling agent, an epoxy compound, a polyisocyanate or a diazonium salt) to the pigment surface may be used and these are described in the following publications and patents:

(1) Kinzoku Sekken no Seishitsu to Oyo (Properties and Applications of Metal Soap), Saiwai Shobo;

(2) Insatsu Ink Insatsu (Printing Ink Printing), CMC Shuppan (1984);

(3) Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Shuppan (1986);

(4) U.S. Patents 5,554,739 and 5,571,311; and

(5) JP-A-9-151342, JP-A-10-140065, JP-A-10-292143 and JP-A-11-166145.

Particularly, self-dispersible pigments prepared by allowing a diazonium salt to act on carbon black described in U.S. patents of (4) and capsulated pigments prepared by the method described in Japanese patent publications of (5) are effective, because dispersion stability can be obtained

without using an excess dispersant in the ink.

In the present invention, the pigment may be dispersed by further using a dispersant. Various known dispersants can be used according to the pigment used, for example, a surfactant-type low molecular dispersant or a polymer-type dispersant can be used. Examples of the dispersant include those described in JP-A-3-69949 and European Patent 549486. In using the dispersant, a pigment derivative called synergist may also be added so as to accelerate the adsorption of dispersant to the pigment.

The particle size of the pigment which can be used in the present invention is, after dispersion, preferably from 0.01 to 10 μm, more preferably from 0.05 to 1 μm.

As for the method of dispersing the pigment, known dispersion techniques used for the production of ink or toner can be used. Examples of the dispersing machine include vertical or horizontal agitator mill, attritor, colloid mill, ball mill, three-roll mill, pearl mill, super-mill, impeller, disperser, KD mill, dynatron and pressure kneader. These are described in detail in Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Shuppan (1986).

Other components which can be contained in each constituent ink of the ink set for inkjet recording of the present invention are described below.

Each constituent ink may contain a surfactant and by containing a surfactant, the liquid properties of ink can be controlled to provide excellent effects such as enhancement of ejection stability of ink, improvement of water resistance of image, and prevention of bleeding of printed ink.

Examples of the surfactant include anionic surfactants such as sodium dodecylsulfate, sodium dodecyloxysulfonate and sodium alkylbenzenesulfonate, cationic surfactants such as cetylpyridinium chloride, trimethylcetylammonium chloride and tetrabutylammonium chloride, and nonionic surfactants such as polyoxyethylene nonylphenyl ether, polyoxyethylene naphthyl ether and polyoxyethylene octylphenyl ether. Among these, nonionic surfactants are preferred.

The surfactant content is from 0.001 to 15 weight %, preferably from 0.005 to 10 weight %, more preferably from 0.01 to 5 weight %, based on the ink.

Each constituent ink can be prepared by dissolving and/or dispersing the above-described phthalocyanine dye and surfactant in an aqueous medium. The term "aqueous medium" as used in the present invention means water or a mixture of water and a small amount of water-miscible organic solvent, where additives such as wetting agent, stabilizer and antiseptic are added, if desired.

Examples of the water-miscible organic solvent which can be used in the present invention include alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, tert-butanol, pentanol, hexanol, cyclohexanol, benzyl alcohol), polyhydric alcohols (e.g., ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, butylene glycol, hexanediol, pentanediol, glycerin, hexanetriol, thiodiglycol), glycol derivatives (e.g., ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, triethylene glycol monomethyl ether, ethylene glycol diacetate, ethylene glycol monomethyl ether acetate, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, ethylene glycol monophenyl ether), amines (e.g., ethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, morpholine, N-ethylmorpholine, ethylenediamine, diethylenetriamine, triethylenetetramine, polyethyleneimine, tetramethylpropylenediamine) and other polar solvents (e.g., formamide, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, sulfolane, 2-pyrrolidone, N-methyl-2-pyrrolidone,

N-vinyl-2-pyrrolidone, 2-oxazolidone, 1,3-dimethyl-2-imidazolidinone, acetonitrile, acetone). These water-miscible organic solvents can be used in combination of two or more thereof.

In the case where the phthalocyanine dye or other dye usable in the present invention is an oil-soluble dye, the ink can be prepared by dissolving the oil-soluble dye in a high boiling point organic solvent and emulsion-dispersing it in an aqueous medium.

The high boiling point organic solvent for use in the present invention has a boiling point of 150°C or more, preferably 170°C or more.

Examples of the high boiling point organic solvent include phthalic acid esters (e.g., dibutyl phthalate, dioctyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl) isophthalate, bis(1,1-diethylpropyl) phthalate), esters of phosphoric acid or phosphone (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyldiphenyl phosphate, dioctylbutyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, di-2-ethylhexylphenyl phosphate), benzoic acid esters (e.g., 2-ethylhexyl benzoate, 2,4-dichlorobenzoate, dodecyl benzoate, 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecanamide,

N,N-diethyllaurylamide), alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-tert-amylphenol), aliphatic esters (e.g., dibutoxyethyl succinate, di-2-ethylhexyl succinate, 2-hexyldecyl tetradecanoate, tributyl citrate, diethyl azelate, isostearyl lactate, trioctyl citrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), chlorinated paraffins (e.g., paraffins having a chlorine content of 10 to 80%), trimesic acid esters (e.g., tributyl trimesate), dodecylbenzene, diisopropylnaphthalene, phenols (e.g., 2,4-di-tert-amyl-phenol, 4-dodecyloxyphenol, 4-dodecyloxycarbonylphenol, 4-(4-dodecyloxyphenylsulfonyl)phenol), carboxylic acids (e.g., 2-(2,4-di-tert-amylphenoxy)butyric acid, 2-ethoxyoctane-decanoic acid) and alkylphosphoric acids (e.g., di-(2-ethylhexyl)phosphoric acid and diphenylphosphoric acid). The high boiling point organic solvent can be used in an amount of, in terms of weight ratio to the oil-soluble dye, from 0.01 to 3 times, preferably from 0.01 to 1.0 times.

These high boiling point organic solvents may be used individually or as a mixture of several kinds [for example, tricresyl phosphate and dibutyl phthalate, trioctyl phosphate and di(2-ethylhexyl) sebacate, or dibutyl phthalate and poly(N-tert-butylacrylamide)].

Examples of the high boiling point organic solvent for use in the present invention, other than the above-

described compounds, and/or the synthesis method of these high boiling point organic solvents are described in U.S. Patents 2,322,027, 2,533,514, 2,772,163, 2,835,579, 3,594,171, 3,676,137, 3,689,271, 3,700,454, 3,748,141, 3,764,336, 3,765,897, 3,912,515, 3,936,303, 4,004,928, 4,080,209, 4,127,413, 4,193,802, 4,207,393, 4,220,711, 4,239,851, 4,278,757, 4,353,979, 4,363,873, 4,430,421, 4,430,422, 4,464,464, 4,483,918, 4,540,657, 4,684,606, 4,728,599, 4,745,049, 4,935,321 and 5,013,639, EP-A-276319, EP-A-286253, EP-A-289820, EP-A-309158, EP-A-309159, EP-A-309160, EP-A-509311, EP-A-510576, East German Patents 147,009, 157,147, 159,573 and 225,240A, British Patent 2091124A, JP-A-48-47335, JP-A-50-26530, JP-A-51-25133, JP-A-51-26036, JP-A-51-27921, JP-A-51-27922, JP-A-51-149028, JP-A-52-46816, JP-A-53-1520, JP-A-53-1521, JP-A-53-15127, JP-A-53-146622, JP-A-54-91325, JP-A-54-106228, JP-A-54-118246, JP-A-55-59464, JP-A-56-64333, JP-A-56-81836, JP-A-59-204041, JP-A-61-84641, JP-A-62-118345, JP-A-62-247364, JP-A-63-167357, JP-A-63-214744, JP-A-63-301941, JP-A-64-9452, JP-A-64-9454, JP-A-64-68745, JP-A-1-101543, JP-A-1-102454, JP-A-2-792, JP-A-2-4239, JP-A-2-43541, JP-A-4-29237, JP-A-4-30165, JP-A-4-232946 and JP-A-4-346338.

The high boiling point organic solvent is used in an amount of, in terms of weight ratio to the oil-soluble dye, from 0.01 to 3.0 times, preferably from 0.01 to 1.0 times.

In the present invention, the oil-soluble dye or high boiling point organic solvent is used by emulsion-dispersing it in an aqueous medium. Depending on the case, a low boiling point organic solvent may be used at the emulsion-dispersion in view of emulsifiability. The low boiling point organic solvent is an organic solvent having a boiling point of about 30 to 150°C under atmospheric pressure. Preferred examples thereof include, but are not limited to, esters (e.g., ethyl acetate, butyl acetate, ethyl propionate, β-ethoxyethyl acetate, methylcellosolve acetate), alcohols (e.g., isopropyl alcohol, n-butyl alcohol, secondary butyl alcohol), ketones (e.g., methyl isobutyl ketone, methyl ethyl ketone, cyclohexanone), amides (e.g., dimethylformamide, N-methylpyrrolidone) and ethers (e.g., tetrahydrofuran, dioxane).

In the emulsion-dispersion, an oil phase obtained by dissolving the dye in a high boiling organic solvent or depending on the case, in a mixed solvent of a high boiling organic solvent and a low boiling organic solvent is dispersed in an aqueous phase mainly comprising water to form fine oil droplets of the oil phase. At this time, in either one or both of the aqueous phase and the oil phase, additives described later, such as surfactant, wetting agent, dye stabilizer, emulsification stabilizer, antiseptic and fungicide, can be added, if desired.

In the general emulsification method, an oil phase is added to an aqueous phase, but a so-called phase inversion emulsification method of adding dropwise an aqueous phase in an oil phase can also be preferably used.

In the present invention, various surfactants can be used at the emulsion-dispersion. Preferred examples thereof include anionic surfactants such as fatty acid salt, alkylsulfuric ester salt, alkylbenzenesulfonate, alkylnaphthalenesulfonate, dialkylsulfosuccinate, alkylphosphoric ester salt, naphthalenesulfonic acid formalin condensate and polyoxyethylene alkylsulfuric ester salt, and nonionic surfactants such as polyoxyethylene alkyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkylamine, glycerin fatty acid ester and oxyethylene oxypropylene block copolymer. Also, SURFYNOLS (produced by Air Products & Chemicals), which are an acetylene-base polyoxyethylene oxide surfactant, are preferably used. Furthermore, amine oxide-type amphoteric surfactants such as N,N-dimethyl-N-alkylamine oxide are preferred. In addition, surfactants described in JP-A-59-157636 (pages (37) to (38)) and Research Disclosure, No. 308119 (1989) can also be used.

For the purpose of stabilizing the dispersion

immediately after emulsification, a water-soluble polymer may be added in combination with the surfactant. Preferred examples of the water-soluble polymer include polyvinyl alcohol, polyvinylpyrrolidone, polyethylene oxide, polyacrylic acid, polyacrylamide and copolymers thereof. Other than these, natural water-soluble polymers such as polysaccharides, casein and gelatin are also preferably used. Furthermore, for the stabilization of dye dispersion, a polymer which does not substantially dissolve in an aqueous medium, such as polyvinyl, polyurethane, polyester, polyamide, polyurea and polycarbonate obtained by the polymerization of acrylic acid esters, methacrylic acid esters, vinyl esters, acrylamides, methacrylamides, olefins, styrenes, vinyl ethers or acrylonitriles, can also be used in combination. This polymer preferably contains $-SO^{2-}$ or $-COO^{-}$. In the case of using this polymer which does not substantially dissolve in an aqueous medium, the polymer is preferably used in an amount of 20 weight % or less, more preferably 10 weight % or less, based on the high boiling point organic solvent.

In preparing an aqueous ink by dispersing the oil-soluble dye or high boiling point organic solvent through emulsion-dispersion, the control of particle size is important. In order to elevate the color purity or density of an image formed by the inkjet recording, it is essential

to reduce the average particle size. The average particle size is, in terms of the volume average particle size, preferably 1 μm or less, more preferably from 5 to 100 nm.

The volume average particle size and particle size distribution of the dispersed particles can be easily measured by a known method such as static light scattering method, dynamic light scattering method, centrifugal precipitation method and the method described in Jikken Kagaku Koza (Lecture of Experimental Chemistry), 4th ed., pp. 417-418. For example, the ink is diluted with distilled water to a particle concentration of 0.1 to 1 weight %, then, the particle size can be easily measured by a commercially available volume average particle size measuring apparatus (for example, Microtrac UPA (manufactured by Nikkiso K.K.)). The dynamic light scattering method utilizing the laser Doppler effect is particularly preferred because even a small particle size can be measured.

The volume average particle size is an average particle size weighted with the particle volume and is obtained by multiplying the diameter of individual particles in the gathering of particles by the volume of the particle and dividing the sum total of the obtained values by the total volume of the particles. The volume average particle size is described in Soichi Muroi,

Kobunshi Latex no Kagaku (Chemistry of Polymer Latex), page 119, Kobunshi Kanko Kai.

Also, it is revealed that the presence of coarse particles greatly affects the printing performance. More specifically, the coarse particle clogs the nozzle of head or even if the nozzle is not clogged, forms a soil to bring about ejection failure or ejection slippage of ink and this seriously affects the printing performance. In order to prevent these troubles, it is important to reduce the number of particles having a particle size of 5 μm or more to 10 or less and the number of particles having a particle size of 1 μm or more to 1,000 or less, in 1 μl of ink prepared.

For removing these coarse particles, a known method such as centrifugal separation or microfiltration can be used. This separation step may be performed immediately after the emulsion-dispersion or may be performed immediately before filling the ink in an ink cartridge after various additives such as wetting agent and surfactant are added to the emulsified dispersion.

A mechanically emulsifying apparatus effective for reducing the average particle size and eliminating coarse particles can be used.

As for the emulsifying apparatus, known apparatuses such as simple stirrer, impeller stirring system, in-line

stirring system, mill system (e.g., colloid mill) and ultrasonic system can be used, but a high-pressure homogenizer is particularly preferred.

The mechanism of the high-pressure homogenizer is described in detail in U.S. Patent 4,533,254 and JP-A-6-47264. Examples of the commercially available apparatus include Gaulin Homogenizer (manufactured by A.P.V Gaulin Inc.), Microfluidizer (manufactured by Microfluidex Inc.) and Altimizer (produced by Sugino Machine).

The high-pressure homogenizer with a mechanism of pulverizing particles in an ultrahigh pressure jet stream recently described in U.S. Patent 5,720,551 is particularly effective for the emulsion-dispersion of the present invention. Examples of the emulsifying apparatus using this ultrahigh pressure jet stream include DeBEE2000 (manufactured by BEE International Ltd.).

In performing the emulsification by a high-pressure emulsion-dispersing apparatus, the pressure is 50 MPa or more, preferably 60 MPa or more, more preferably 180 MPa or more.

A method of using two or more emulsifying apparatuses, for example, by performing the emulsification in a stirring emulsifier and then passing the emulsified product through a high-pressure homogenizer is particularly preferred. Also, a method of once performing the emulsion-dispersion

by such an emulsifying apparatus and after adding additives such as wetting agent and surfactant, again passing the dispersion through a high-pressure homogenizer during filling of the ink into a cartridge is preferred.

In the case of containing a low boiling point organic solvent in addition to the high boiling point organic solvent, the low boiling point solvent is preferably removed in view of stability of the emulsified product, safety and hygiene. For removing the low boiling point solvent, various known methods can be used according to the kind of the solvent, such as evaporation, vacuum evaporation and ultrafiltration. This removal of the low boiling point organic solvent is preferably performed as soon as possible immediately after the emulsification.

In the inkjet recording ink set of the present invention or a constituent ink thereof, additives such as drying inhibitor for preventing clogging due to drying of ink at the ejection port, penetration accelerator for more successfully penetrating the ink into paper, ultraviolet absorbent, antioxidant, viscosity adjusting agent, surface tension adjusting agent, dispersant, dispersion stabilizer, fungicide, rust inhibitor, pH adjusting agent, defoaming agent and chelating agent, may be appropriately selected and used in an appropriate amount.

The drying inhibitor for use in the present invention

is preferably a water-soluble organic solvent having a vapor pressure lower than water. Specific examples thereof include polyhydric alcohols as represented by ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, thiodiglycol, dithiodiglycol, 2-methyl-1,3-propanediol, 1,2,6-hexanetriol, acetylene glycol derivative, glycerin and trimethylolpropane; lower alkyl ethers of polyhydric alcohol, such as ethylene glycol monomethyl(or ethyl) ether, diethylene glycol monomethyl(or ethyl) ether and triethylene glycol monoethyl(or butyl) ether; heterocyclic rings such as 2-pyrrolidone, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone and N-ethylmorpholine; sulfur-containing compounds such as sulfolane, dimethylsulfoxide and 3-sulfolene; polyfunctional compounds such as diacetone alcohol and diethanolamine; and urea derivatives. Among these, polyhydric alcohols such as glycerin and diethylene glycol are preferred. These drying inhibitors may be used individually or in combination of two or more thereof. In the ink, the drying inhibitor is preferably contained in an amount of 10 to 50 weight %.

Examples of the penetration accelerator which can be used in the present invention include alcohols such as ethanol, isopropanol, butanol, di(tri)ethylene glycol monobutyl ether and 1,2-hexanediol, sodium laurylsulfate,

sodium oleate and nonionic surfactants. A sufficiently high effect can be obtained by adding from 10 to 30 weight % of the penetration accelerator in the ink. The penetration accelerator is preferably used in an amount of causing no blurring of printed letter or no print through.

Examples of the ultraviolet absorbent which can be used in the present invention for improving the preservability of image include benzotriazole-base compounds described in JP-A-58-185677, JP-A-61-190537, JP-A-2-782, JP-A-5-197075 and JP-A-9-34057, benzophenone-base compounds described in JP-A-46-2784, JP-A-5-194483 and U.S. Patent 3,214,463, cinnamic acid-base compounds described in JP-B-48-30492 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-B-56-21141 and JP-A-10-88106, triazine-base compounds described in JP-A-4-298503, JP-A-8-53427, JP-A-8-239368, JP-A-10-182621 and JP-T-8-501291, compounds described in Research Disclosure No. 24239, and compounds of absorbing ultraviolet light and emitting fluorescent light, so-called fluorescent brightening agents, as represented by stilbene-base compounds and benzoxazole-base compounds.

As for the antioxidant which is used in the present invention for improving the preservability of image, various organic or metal complex-base discoloration inhibitors can be used. Examples of the organic

discoloration inhibitor include hydroquinones, alkoxy-phenols, dialkoxyphenols, phenols, anilines, amines, indanes, chromans, alkoxyanilines and heterocyclic rings. Examples of the metal complex include nickel complex and zinc complex. More specifically, compounds described in patents cited in Research Disclosure, Nos. 17643 (Items VII-I to VII-J), 15162, 18716 (page 650, left column), 36544 (page 527), 307105 (page 872) and 15162, and compounds included in formulae of representative compounds and in exemplary compounds described in JP-A-62-215272 (pages 127 to 137) can be used.

Examples of the fungicide for use in the present invention include sodium dehydroacetate, sodium benzoate, sodium pyridinethione-1-oxide, ethyl p-hydroxybenzoate, 1,2-benzisothiazolin-3-one and salts thereof. In the ink, the fungicide is preferably used in an amount of 0.02 to 5.00 weight %.

The fungicide is described in detail, for example, in Bokin Bobai Zai Jiten (Dictionary of Microbicide and Fungicide), compiled by Nippon Bokin Bobai Gakkai Jiten Henshu Iinkai.

Examples of the rust inhibitor include acidic sulfite, sodium thiosulfate, ammonium thioglycolate, diisopropyl-ammonium nitrite, pentaerythritol tetranitrate, dicyclohexylammonium nitrite and benzotriazole. In the ink,

the rust inhibitor is preferably used in an amount of 0.02 to 5.00 weight %.

The pH adjusting agent for use in the present invention can be suitably used for adjusting the pH and imparting dispersion stability. The pH of the ink is preferably adjusted to 4 to 11 at 25°C. If the pH is less than 4, the solubility of dye decreases to readily cause clogging of a nozzle, whereas if it exceeds 11, the water resistance tends to deteriorate. Examples of the pH adjusting agent include organic bases and inorganic alkalis for giving a basic pH, and organic acids and inorganic acids for giving an acidic pH.

Examples of the organic base include triethanolamine, diethanolamine, N-methyldiethanolamine and dimethylethanolamine. Examples of the inorganic alkali include alkali metal hydroxides (e.g., sodium hydroxide, lithium hydroxide, potassium hydroxide), alkali metal carbonates (e.g., sodium carbonate, sodium hydrogencarbonate) and ammonium. Examples of the organic acid include an acetic acid, a propionic acid, a trifluoroacetic acid and an alkylsulfonic acid. Examples of the inorganic acid include a hydrochloric acid, a sulfuric acid and a phosphoric acid.

In the present invention, apart from the above-described surfactants, a nonionic, cationic or anionic surfactant is used as the surface tension adjusting agent.

Examples thereof include anionic surfactants such as fatty acid salt, alkylsulfuric ester salt, alkylbenzenesulfonate, alkylnaphthalenesulfonate, dialkylsulfosuccinate, alkylphosphoric ester salt, naphthalenesulfonic acid formalin condensate and polyoxyethylenealkylsulfuric ester salt, and nonionic surfactants such as polyoxyethylene alkyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkylamine, glycerin fatty acid ester and oxyethylene oxypropylene block copolymer. Also, SURFYNOLS (produced by Air Products & Chemicals), which are an acetylene-base polyoxyethylene oxide surfactant, are preferably used. Furthermore, amine oxide-type amphoteric surfactants such as N,N-dimethyl-N-alkylamine oxide are preferred. In addition, surfactants described in JP-A-59-157636 (pages (37) to (38)) and Research Disclosure, No. 308119 (1989) can also be used.

The surface tension of the ink of the present invention is, with or without use of such a surface tension adjusting agent, preferably from 20 to 60 mN/m, more preferably from 25 to 45 mN/m.

The ink of the present invention preferably has a viscosity of 30 mPa·s or less. The viscosity is more preferably adjusted to 20 mPa·s or less. For the purpose of adjusting the viscosity, a viscosity adjusting agent is

sometimes used. Examples of the viscosity adjusting agent include celluloses, water-soluble polymers such as polyvinyl alcohol, and nonionic surfactants. The viscosity adjusting agent is described in detail in Nendo Chosei Gijutsu (Viscosity Adjusting Technology), Chap. 9, Gijutsu Joho Kyokai (1999), and Inkjet Printer Yo Chemicals (98 Zoho) -Zairyo no Kaihatsu Doko·Tenbo Chosa- (Chemicals for Inkjet Printer (Enlarged Edition of 98) -Survey on Development Tendency·Prospect of Materials-), pp. 162-174, CMC (1997).

In the present invention, if desired, various cationic, anionic or nonionic surfactants described above may be used as a dispersant or a dispersion stabilizer, and fluorine- or silicone-base compounds or chelating agents as represented by EDTA may be used as a defoaming agent.

In preparing the ink solution of the present invention, in the case of a water-soluble ink, the dye is preferably first dissolved in water and thereafter, various solvents and additives are added, dissolved and mixed to provide a uniform ink solution.

For dissolving the dye and the like, various methods such as stirring, ultrasonic irradiation and shaking can be used. Among these, stirring is preferred. In performing the stirring, various systems known in this field can be used, such as flow stirring and stirring utilizing a

shearing force with use of a reversal agitator or a dissolver. Also, a stirring method utilizing a shearing force with the bottom surface of a vessel, such as magnetic stirrer, can be advantageously used.

The recording paper and recording film for use in the image recording method of the present invention are described below. The support which can be used for the recording paper or film is produced, for example, from a chemical pulp such as LBKP and NBKP, a mechanical pulp such as GP, PGW, RMP, TMP, CTMP, CMP and CGP, or a waste paper pulp such as DIP, by mixing, if desired, conventionally known additives such as pigment, binder, sizing agent, fixing agent, cation agent and paper strength increasing agent, and then sheeting the mixture by using various devices such as Fourdrinier paper machine and cylinder paper machine. Other than these supports, synthetic paper or plastic film sheet may be used. The thickness of the support is preferably from 10 to 250 μm and the basis weight is preferably from 10 to 250 g/m^2.

An image-receiving layer and a backcoat layer may be provided on the support as it is to produce an image-receiving material, or after providing a size press or an anchor coat layer by using starch, polyvinyl alcohol or the like, an image-receiving layer and a backcoat layer may be provided to produce an image-receiving material. The

support may be further subjected to a flattening treatment by a calendering device such as machine calender, TG calender and soft calender.

In the present invention, the support is preferably paper or plastic film of which both surfaces are laminated with polyolefin (for example, polyethylene, polystyrene, polyethylene terephthalate, polybutene or a copolymer thereof). In the polyolefin, a white pigment (for example, titanium oxide or zinc oxide) or a tinting dye (for example, cobalt blue, ultramarine or neodymium oxide) is preferably added.

The image-receiving layer provided on the support contains a porous material and an aqueous binder. Also, the image-receiving layer preferably contains a pigment and the pigment is preferably a white pigment. Examples of the white pigment include inorganic white pigments such as calcium carbonate, kaolin, talc, clay, diatomaceous earth, synthetic amorphous silica, aluminum silicate, magnesium silicate, calcium silicate, aluminum hydroxide, alumina, lithopone, zeolite, barium sulfate, calcium sulfate, titanium dioxide, zinc sulfide and zinc carbonate, and organic pigments such as styrene-base pigment, acryl-base pigment, urea resin and melamine resin. Among these, porous inorganic white pigments are preferred, and synthetic amorphous silica and the like having a large pore

area are more preferred. The synthetic amorphous silica may be either a silicic acid anhydride obtained by a dry production process or a silicic acid hydrate obtained by a wet production process, but a silicic acid hydrate is preferred. These pigments may be used in combination of two or more thereof.

Examples of the aqueous binder contained in the image-receiving layer include water-soluble polymers such as polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose, polyvinylpyrrolidone, polyalkylene oxide and polyalkylene oxide derivative, and water-dispersible polymers such as styrene butadiene latex and acryl emulsion. These aqueous binders can be used individually or in combination of two or more thereof. Among these, polyvinyl alcohol and silanol-modified polyvinyl alcohol are preferred in the present invention in view of adhesion to the pigment and separation resistance of the image-receiving layer.

The image-receiving layer may contain a mordant, a water-proofing agent, a light fastness enhancer, a surfactant, a hardening agent and other additives in addition to the pigment and aqueous binder.

The mordant added to the image-receiving layer is preferably immobilized and for this purpose, a polymer

mordant is preferably used.

The polymer mordant is described in JP-A-48-28325, JP-A-54-74430, JP-A-54-124726, JP-A-55-22766, JP-A-55-142339, JP-A-60-23850, JP-A-60-23851, JP-A-60-23852, JP-A-60-23853, JP-A-60-57836, JP-A-60-60643, JP-A-60-118834, JP-A-60-122940, JP-A-60-122941, JP-A-60-122942, JP-A-60-235134, JP-A-1-161236 and U.S. Patents 2,484,430, 2,548,564, 3,148,061, 3,309,690, 4,115,124, 4,124,386, 4,193,800, 4,273,853, 4,282,305 and 4,450,224. An image-receiving material containing the polymer mordant described in JP-A-1-161236 (pages 212 to 215) is particularly preferred. When the polymer mordant described in this patent publication is used, an image having excellent pictorial quality can be obtained and at the same time, the light fastness of the image is improved.

The water-proofing agent is effective for obtaining a water-resistant image. The water-proofing agent is preferably a cationic resin. Examples of the cationic resin include polyamidopolyamine epichlorohydrin, polyethyleneimine, polyaminesulfone, poly-dimethyldiallyl-ammonium chloride, cationic polyacrylamide and colloidal silica. Among these cationic resins, polyamidopolyamine epichlorohydrin is preferred. The content of the cationic resin is preferably from 1 to 15 weight %, more preferably from 3 to 10 weight %, based on the entire solid content of

the ink-receiving layer.

Examples of the light fastness enhancer include zinc sulfate, zinc oxide, hindered amine-base antioxidant and benzotriazole-base ultraviolet absorbent such as benzophenone. Among these, zinc sulfate is preferred.

The surfactant functions as a coating aid, a releasability improver, a slipperiness improver or an antistatic agent. This surfactant is described in JP-A-62-173463 and JP-A-62-183457.

Instead of the surfactant, an organofluoro compound may be used. The organofluoro compound is preferably hydrophobic. Examples of the organofluoro compound include fluorine-containing surfactants, oily fluorine-base compounds (for example, fluorine oil) and solid fluorine compound resins (for example, ethylene tetrafluoride resin). The organofluoro compound is described in JP-B-57-9053 (columns 8 to 17), JP-A-61-20994 and JP-A-62-135826.

Examples of the hardening agent which can be used include the materials described in JP-A-1-161236 (page 222).

Other examples of the additive added to the image-receiving layer include a pigment dispersant, a thickener, a defoaming agent, a dye, a fluorescent brightening agent, an antiseptic, a pH adjusting agent, a matting agent and a hardening agent. The image-receiving layer may be composed of one layer or two layers.

In the recording paper or film, a backcoat layer may also be provided. Examples of the component which can be added to this layer include a white pigment, an aqueous binder and other components.

Examples of the white pigment contained in the backcoat layer include white inorganic pigments such as precipitated calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic amorphous silica, colloidal silica, colloidal alumina, pseudo-boehmite, aluminum hydroxide, alumina, lithopone, zeolite, hydrolyzed halloysite, magnesium carbonate and magnesium hydroxide, and organic pigments such as styrene-base plastic pigment, acryl-base plastic pigment, polyethylene, microcapsule, urea resin and melamine resin.

Examples of the aqueous binder contained in the backcoat layer include water-soluble polymers such as styrene/maleate copolymer, styrene/acrylate copolymer, polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose and polyvinylpyrrolidone, and water-dispersible polymers such as styrene butadiene latex and acryl emulsion. Other examples of the component

contained in the backcoat layer include a defoaming agent, a foam inhibitor, a dye, a fluorescent brightening agent, an antiseptic and a water-proofing agent.

In a constituent layer (including the back layer) of the inkjet recording paper or film, a polymer fine particle dispersion may be added. The polymer fine particle dispersion is used for the purpose of improving film properties, for example, stabilizing the dimension or preventing the curling, adhesion or film cracking. The polymer fine particle dispersion is described in JP-A-62-245258, JP-A-62-1316648 and JP-A-62-110066. When a polymer fine particle dispersion having a low glass transition temperature (40°C or less) is added to a layer containing a mordant, the layer can be prevented from cracking or curling. The curling can be prevented also by adding a polymer fine particle dispersion having a high glass transition temperature to the back layer.

The present invention is not limited in the inkjet recording system and used for a known system, for example, an electric charge control system of jetting out the ink by utilizing the electrostatic induction force, a drop-on-demand system (pressure pulse system) utilizing an oscillation pressure of a piezoelectric element, an acoustic inkjet system of converting electric signals into acoustic beams, irradiating the beams on the ink and

jetting out the ink by utilizing the radiation pressure, and a thermal inkjet (bubble jet) system of heating the ink to form a bubble and utilizing the pressure generated.

The inkjet recording system includes a system of ejecting a large number of small-volume ink droplets of a so-called photo ink having a low concentration, a system of improving the pictorial quality by using a plurality of inks having substantially the same color hue but differing in the concentration, and a system using a colorless transparent ink.

The inkjet recording ink of the present invention can also be used for uses other than the inkjet recording, such as a material for display image, an image-forming material for interior decoration, and an image-forming material for outdoor decoration.

The material for display image indicates various materials such as poster, wallpaper, ornamental goods (e.g., ornament, doll), handbill for commercial advertisement, wrapping paper, wrapping material, paper bag, vinyl bag, package material, billboard, image drawn on or attached to the side face of traffic (e.g., automobile, bus, electric car), and clothing with a logo. In the case of using the dye of the present invention as a material for forming a display image, the image includes not only a strict image but also all patterns by a dye, which can be perceived by a

human, such as abstract design, letter and geometrical pattern.

The material for interior decoration indicates various materials such as wallpaper, ornamental goods (e.g., ornament, doll), luminaire member, furniture member and design member of floor or ceiling. In the case of using the dye of the present invention as a material for forming an image, the image includes not only a strict image but also all patterns by a dye, which can be perceived by a human, such as abstract design, letter and geometrical pattern.

The material for outdoor decoration indicates various materials such as wall material, roofing material, billboard, gardening material, outdoor ornamental goods (e.g., ornament, doll) and outdoor luminaire member. In the case of using the dye of the present invention as a material for forming an image, the image includes not only a strict image but also all patterns by a dye, which can be perceived by a human, such as abstract design, letter and geometrical pattern.

In these uses, examples of the medium on which the pattern is formed include various materials such as paper, fiber, cloth (including non-woven fabric), plastic, metal and ceramic. Examples of the dyeing form include mordanting, printing and fixing of a colorant in the form

of a reactive dye having introduced thereinto a reactive group. Among these, preferred is dyeing by mordanting.

[Examples]

The present invention is described below by referring to Examples, but the present invention is not limited thereto.

(Example 1)

<Production of Ink Set Sample>

Deionized water was added to the following components to make 1 liter and the resulting solution was stirred for 1 hour under heating at 30 to 40°C. Thereafter, the pH was adjusted to 6.0 by using 1 mol/liter of hydrochloric acid or potassium hydroxide and then the solution was filtered under reduced pressure through a microfilter having an average pore size of 0.25 μm to prepare a magenta ink solution (M-1).

Magenta dye of the present invention (Compound a-36)	24 g/liter
Diethylene glycol	150 g/liter
Urea	37 g/liter
Glycerin	130 g/liter
Triethylene glycol monobutyl ether	130 g/liter
Triethanolamine	6.9 g/liter
Benzotriazole	0.08 g/liter
PROXEL XL2	3.5 g/liter

Surfynol STG 10 g/liter

Also, 7 kinds of light magenta inks for Ink Samples 102 to 108 shown in Table 1 were produced by changing the amount of the magenta dye (a-36) in the formulation above as shown in Table 1 to vary the absorbance. The absorbance was measured by 10,000-fold diluting the ink sample with the ink solvent.

Also, as a reference sample, the magenta ink and light magenta ink in the ink set for PM-950C of Seiko Epson Corporation were used as-is (Sample 101).

Table 1

Ink No.	Light Magenta Ink (concentration)	Magenta Ink
101 (Reference Example)	ink of PM-950C	ink of PM-950C
102 (Comparative Example)	1/25 of M-1	M-1
103 (Comparative Example)	2/3 of M-1	M-1
104 (Invention)	1/12 of M-1	M-1
105 (Invention)	1/6 of M-1	M-1
106 (Invention)	1/4 of M-1	M-1
107 (Invention)	1/3 of M-1	M-1
108 (Invention)	2/5 of M-1	M-1

These Ink Set Samples 101 to 108 each was then filled in the magenta ink·light magenta part of the ink cartridge of Inkjet Printer PM-950C (manufactured by Seiko Epson Corporation) and in the same printer, an image was printed on inkjet paper Photo Gloss Paper EX produced by Fuji Photo

Film Co., Ltd. The image obtained was evaluated on the pictorial quality and fastness. Since inks differing in the concentration were used, the printing was performed after adjusting the magenta density on a software.

<Evaluation>

Pictorial Quality:

As for the pictorial quality, a continuous gradation pattern (reflection density: 0.10 to 2.0) of gray was prepared by color inks of C, M and Y and the gradation reproducibility was evaluated with an eye and rated A, B or C.

Image Preservability:

As for the image preservability, a magenta solid image (a color picture having almost uniform density with no distribution) printed sample was prepared and subjected to the following evaluations.

(1) In the evaluation of light fastness, the image density Ci immediately after printing was measured by X-Rite 310 and after the image was irradiated with xenon light (85,000 lx) for 10 days by using a weather meter manufactured (Weather-O-meter, manufactured by Atlas Electronic Devices, Inc., USA), the image density Cf was again measured. Then, the dye residual ratio (Cf/Ci*100) was determined and evaluated. The dye residual ratio was evaluated at three points having a reflection density of 1,

1.5 and 2. The sample was rated A when the dye residual ratio was 70% or more at any density, rated B when less than 70% at two points, and rated C when less than 70% at all points.

(2) In the evaluation of heat fastness, the density was measured by X-Rite 310 before and after the sample was stored for 10 days under the conditions of 80°C and 70% RH, and the dye residual ratio was determined and evaluated. The dye residual ratio was evaluated at three points having a reflection density of 1, 1.5 and 2. The sample was rated A when the dye residual ratio was 90% or more at any density, rated B when less than 90% at two points, rated C when less than 90% at all points, and rated D when discoloration or the like was observed.

(3) In the evaluation of ozone resistance, the photo gloss paper having formed thereon the image was left standing for 7 days in a box set to an ozone gas concentration of 0.5 ppm and the image density before and after standing in the ozone gas atmosphere was measured by a reflection densitometer (X-Rite 310TR) and evaluated as a dye residual ratio. The reflection density was measured at three points of 1, 1.5 and 2.0. The ozone gas concentration in the box was set by using an ozone gas monitor (Model OZG-EM-01) manufactured by APPLICS.

The sample was rated on a three-stage scale, namely,

rated A when the dye residual ratio was 80% or more at any density, rated B when less than 80% at one or two point(s), and rated C when less than 70% at all points.

The results obtained are shown in Table 2 below.

Table 2

Ink No.	Gradation Reproducibility	Light Fastness	Heat Fastness	Ozone Resistance
101 (Reference Example)	A	B	B	C
102 (Comparative Example)	C	A	A	A
103 (Comparative Example)	C	A	A	A
104 (Invention)	B	A	A	A
105 (Invention)	A	A	A	A
106 (Invention)	A	A	A	A
107 (Invention)	A	A	A	A
108 (Invention)	A	A	A	A

As seen from Table 2, the ink set of the present invention is excellent in both gradation reproducibility and weather resistance (fastness to light, heat and ozone) and satisfying both the pictorial quality and the fastness.

(Example 2)

<Production of Ink Set Sample>

Deionized water was added to the following components to make 1 liter and the resulting solution was stirred for 1 hour under heating at 30 to 40°C. Thereafter, the pH was

adjusted to 6.0 by using 1 mol/liter of hydrochloric acid or potassium hydroxide and then the solution was filtered under reduced pressure through a microfilter having an average pore size of 0.25 μm to prepare a cyan ink solution (C-1).

Cyan dye of the present invention (Compound 154)	68 g/liter
Diethylene glycol	150 g/liter
Urea	37 g/liter
Glycerin	130 g/liter
Triethylene glycol monobutyl ether	130 g/liter
Triethanolamine	6.9 g/liter
Benzotriazole	0.08 g/liter
PROXEL XL2	3.5 g/liter
Surfynol STG	10 g/liter

Also, 7 kinds of light cyan inks (Samples 102 to 108) shown in Table 3 were produced by changing the amount of the cyan dye in the formulation above to vary the absorbance. The absorbance was measured by 10,000-fold diluting the ink sample with the ink solvent.

Also, as a reference sample for comparison, the cyan ink and light cyan ink in the ink set for PC-950C of Seiko Epson Corporation were used as-is (see, Table 3).

Table 3

Ink No.	Light Cyan Ink (absorbance)	Cyan Ink
101 (Reference Example)	ink of PC-950C	ink of PC-950C
102 (Comparative Example)	1/25 of C-1	C-1
103 (Comparative Example)	2/3 of C-1	C-1
104 (Invention)	1/12 of C-1	C-1
105 (Invention)	1/6 of C-1	C-1
106 (Invention)	1/4 of C-1	C-1
107 (Invention)	1/3 of C-1	C-1
108 (Invention)	2/5 of C-1	C-1

These Inks 101 to 108 each was then filled in the cyan ink·light cyan part of the ink cartridge of Inkjet Printer PC-950C (manufactured by Seiko Epson Corporation) and in the same printer, an image was printed on inkjet paper Photo Gloss Paper EX produced by Fuji Photo Film Co., Ltd. The image obtained was evaluated on the pictorial quality and fastness. Since inks differing in the concentration were used, the printing was performed after adjusting the cyan density on a software.

<Evaluation of Dye>

The evaluation with an eye of the pictorial quality by taking notice of the gradation reproducibility and the evaluation on a three-stage scale of A, B and C of the image preservability in view of light fatness, heat fastness and ozone resistance were performed by the methods

described in Example 1.

The results obtained are shown in Table 4 below.

Table 4

Ink No.	Gradation Reproducibility	Light Fastness	Heat Fastness	Ozone Resistance
101 (Reference Example)	A	B	A	C
102 (Comparative Example)	C	A	A	A
103 (Comparative Example)	C	A	A	A
104 (Invention)	B	A	A	A
105 (Invention)	A	A	A	A
106 (Invention)	A	A	A	A
107 (Invention)	A	A	A	A
108 (Invention)	A	A	A	A

As seen from Table 4, the ink set of the present invention is excellent in both gradation reproducibility and weather resistance (fastness to light, heat and ozone) and satisfying both the pictorial quality and the image fastness.

INDUSTRIAL APPLICABILITY

As described in the foregoing pages, an inkjet recording image with high quality of recording image and excellent preservability of the image drawn can be obtained by an ink set having an absorption wavelength region of 500

to 580 nm or of 580 to 680 nm and being characterized in that based on the absorbance of a dye (or a combination of dyes) in an ink having a maximum dye concentration out of constituent inks, the absorbance of a dye (or a combination of dyes) in another ink is from 1/20 to 1/2.

This ink set can be used for a high pictorial quality inkjet color printer.